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THE USE OF X-RAY DIFFRACTION
PROCEDURES IN
ANALYSIS OF CLAY MINERALS

by

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of the Department of Civil Engineering
in Partial Fulfillment of the
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FOREWARD

This thesis is undertaken in an effort to contribute to the relatively new practice of using X-ray Diffraction procedures in analysis of clay minerals. The main objective is to establish internal standards for the clay minerals and with this to plot calibration curves that may be used in quantitative analysis of unknown clay compounds.

The author wishes to acknowledge the advice and direction provided by Professor E. J. Kilcawley, Head of the Division of Soil Mechanics and Sanitary Engineering, Department of Civil Engineering, Rensselaer Polytechnic Institute, in preparation of this thesis.

In addition, the author is indebted to the Department of Metallurgy under Doctor Arthur A. Burr for providing the x-ray diffraction equipment used, and, is especially indebted to Malcom J. Fraser, Research Associate in Metallurgical Engineering, for his time and technical advice which led to the completion of this thesis.

ABSTRACT

The purpose of this thesis is to apply the internal standard technique of x-ray diffraction to the analysis of clay minerals, outline an analysis procedure for future use, and to apply this procedure to an unknown clay sample.

X-ray diffraction charts were prepared for the three basic clay minerals (Kaolinite, Illite and Montmorillonite) using different ionic saturations for each mineral. The resulting charts enabled the selection of an internal standard material and a diluent that did not interfere with the clay mineral diffraction pattern. Mixtures of clay mineral and internal standard were prepared and run in the X-ray spectrometer. From this, a calibration curve was plotted using the ratio of the weight of clay mineral and internal standard in the mixture and the ratio of their strongest peak intensities from the x-ray strip chart. By plotting this weight ratio against the intensity ratio, calibration curves for quantitative analysis were obtained.

In addition, new and better methods of sample preparation, sample mounting, and x-ray spectrometer procedure were tried and evaluated leading to a proposed step-by-step method of clay mineral analysis which includes sample preparation, quantitative and qualitative analysis.

This procedure was applied to an unknown clay compound obtained from the proposed construction site of the St. Lawrence Seaway Project. The analysis resulting

from this application served to bring out the main conclusion of the thesis, that: the internal standard technique of x-ray diffraction analysis of clay minerals is an excellant research tool, and the procedures evolved from these studies should be used in future clay mineral analysis for best results.

PART I.

INTRODUCTION

A. Historical Review

In recent years the use of X-ray diffraction and X-ray spectrographic techniques as scientific tools has become increasingly important. This is especially true in fields of industry involving minerals such as metallurgy, mining and prospecting, mineral preparation, ceramics, and more recently, the field of soils engineering. Data obtained by x-ray diffraction techniques give the research investigator fundamentals unobtainable by any other technique.

Historically, the fundamental step leading to the use of X-rays in clay mineral research, although not originally applied to minerals, was the discovery by M. Laue[1*] in 1912 that a crystal would serve as a diffraction grating for x-rays.

Investigations from that day forward confirm the conception that crystalline matter is composed of atoms or molecules arranged to form definite families of planes composing a periodic lattice in three dimensions. By considering primary x-rays to be reflected by these planes, W. A. Bragg and W. L. Bragg[2], also in 1912, gave a very simple geometric interpretation of diffraction by a crystal grating.

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* Throughout this thesis, superscript numbers refer to the similarly numbered items in PART VI. (LITERATURE CITED).

They demonstrated that the geometry of a diffracted beam is defined by the relation "$n\lambda = 2d \sin \theta$". This equation has become known as the Bragg equation or Bragg law and is the fundamental equation of present day x-ray diffraction work.

For many years the exact nature of clay minerals was not known, but between 1887 and 1909 LeChatelier[3] and Lowenstein[4] arrived at the conclusion that clay minerals were composed of crystalline materials. This concept was later proven by Hadding in 1922 by use of x-ray diffraction. He found crystalline material in the finest fractions of a series of clays and also found that all clay samples studied seemed to be composed of particles of the same small group of minerals.

The crystalline concept of clay minerals was very important to current soils work, not only because it provides a sound basis for the clay mineral concept, but it also leads to the x-ray diffraction method of observing and explaining the action of clay minerals under varying conditions. This is especially important since clay minerals are now known to be the active portion of soils. The knowledge of the actions of this fraction of the soil under varied conditions (different moisture contents, ionic saturation, type of crystalline structure, etc.) leads to the understanding of many problems encountered. A complete study of this subject may be found in "Soil Physics" by Baver[5].

Qualitative and quantitative analysis procedures

for clay minerals using x-ray diffraction have steadily improved in recent years leading to a better understanding of clay minerals. A basic procedure for clay mineral analysis was published by D. M. C. MacEwan[6] in 1949, and since that time, quantitative analysis has progressed to the point that standard tables have been prepared on many basic clay minerals. These tables are published by the American Society of Testing Materials and are available for use, in conjunction with x-ray patterns, for identification of unknown mineral compounds.

B. Statement of Problem

The problem in working with clay minerals is to identify, qualitatively and quantitatively, the components of an unknown soil sample and thus to predict its actions in nature. Since it has been proven that clay minerals are materials with structures identifiable by crystallographic analysis, it is possible to apply x-ray diffraction procedures to the quantitative and qualitative analysis of an unknown clay sample.

Specifically this thesis is undertaken to provide information on this subject by: (1) establishing calibration curves for the standard clay minerals using the internal standard technique; (2) establish a step-by-step procedure for quantitative and qualitative analysis of clay compounds; (3) actual application of (1) and (2) by trial using an unknown sample.

PART II.

THEORY

A. Crystalline State, Geometry, and Space Lattice

Crystallinity has been recognized since ancient times and with the discovery of x-ray diffraction, it was demonstrated that most solids are crystalline in structure. The exceptions are the amorphus solids that show no crystalline nature at all and include: glasses, resins, opals, etc.

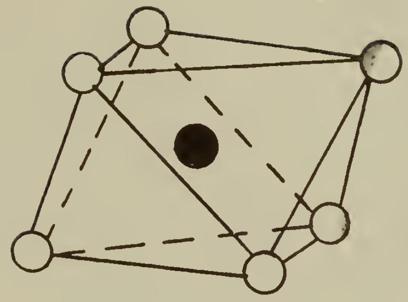
A crystal, by definition, is a homogeneous anisotropic body having the natural shape of a polyhedron. The crystal is composed of atoms or groups of atoms arranged in a regular and repeated pattern, called a space lattice. The smooth plane surfaces bounding a crystal impart to it a characteristic symetry of form. It is rare that a crystal existing in nature yields an absolutely symetrical shape, but usually enough faces show to ascertain the type of crystalline form it represents. One definite characteristic of any crystal is the angle between corresponding faces. These faces may not be of the same size on all crystals, but their interfacial angles will always be constant and characteristic of the species of crystal. By species, the crystals may be classified under six systems: triclinic, monoclinic, orthorhombic, tetragonal, hexagonal, and cubic. Within these systems there are thirty-two possible crystalline forms that can be produced. By investigating the individual crystalline characteristics of a material, including spacing, axis, form,

etc., it is possible to classify the material and use it in identifying unknowns.

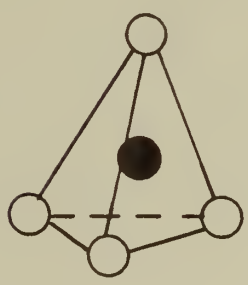
Concerning the clay minerals, it has been found that 98% show definite crystalline structure, the details of which are used in classification and study of the minerals. In general, there are two structural units involved in the make-up of the common clay minerals; these are the octahedron and the tetrahedron(see Figure I (a) and (b). The unit octahedron consists of oxygen atoms surrounding a nucleus of an aluminum atom, and the unit tetrahedron consists of oxygen atoms surrounding a silicon atom.

The unit or basic building block of the clay mineral structure is not able to exist alone due to electrical unbalance, therefore, they combine in all directions and form a final structure known as the space lattice. The resulting equilibrium groupings of crystal units show great diversity with respect to the distance between units and angles between the planes in which they lie. These arrangements can be represented by orderly assemblages of points in three dimensions or, as it is called, the space lattice.

In the clay minerals, the silica unit cells form a sheet or lattice, and the alumina unit cells form another sheet. The different clay minerals are then formed by sheet or lattice make-up: the Kaolinite Group has a 1:1 lattice with one silicon sheet to one alumina sheet; the Illite and Montmorillonite Groups have a 2:1 lattice or two silicon



(a)



(b)

FIGURE I

"Clay Mineral Unit Cells"

sheets to one alumina sheet. Figures II (a) and (b) represent the space lattice of the three major clay minerals: Kaolinite (Figure II (a), Illite and Montmorillonite (Figure II (b). These minerals will be used as standards throughout this thesis. The fact that each has a different and distinguishable structural arrangement leads to their identification by use of x-ray diffraction procedures.

B. X-ray Properties and Production

X-rays were discovered in 1895 by Roentgen and are known to be electromagnetic radiation. They have a relatively short wave length which lies between ultraviolet and gamma radiation in the electromagnetic spectrum. They are produced when fast-moving electrons impinge on matter. With this impingement, there is a transfer of energy from the electrons to the matter, most of which becomes heat energy with the remainder being given off from the matter as the x-radiation. Similiar in nature to light rays, the x-ray exhibits many of the same characteristics of light rays in that they can be refracted, diffracted, and will interfere.

The unit of wave length commonly used in x-ray measurements is the "Angstrom" which is equal to 10^{-8} cm. The x-rays of interest to the diffractionist occur in the range of 0.2 to 2.5 Angstrom. The x-rays increase in hardness or ability to penetrate as the wave length decreases.

X-ray tubes are devices for bringing about the interaction of high-speed electrons with matter for x-ray

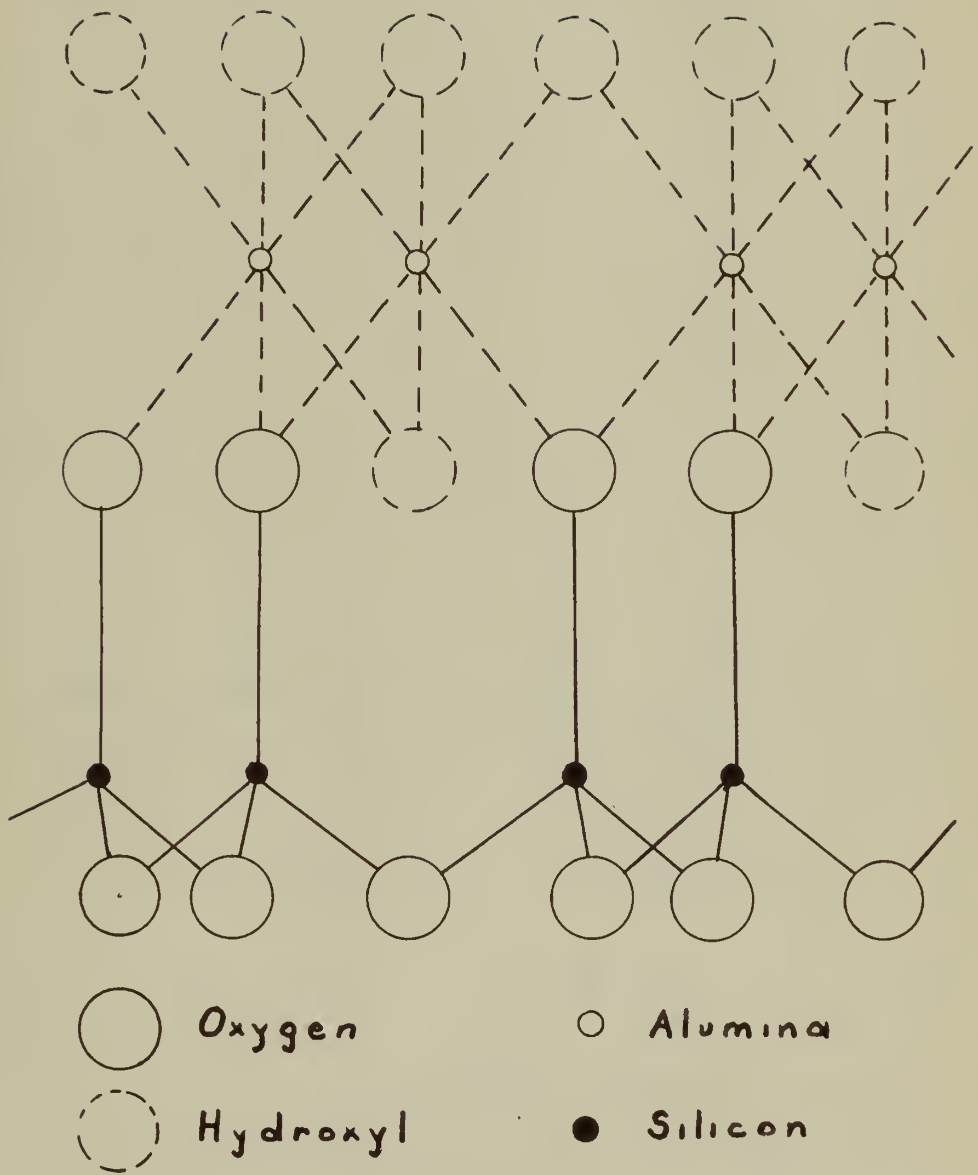


FIGURE II (a)

"Kaolinite Space Lattice"

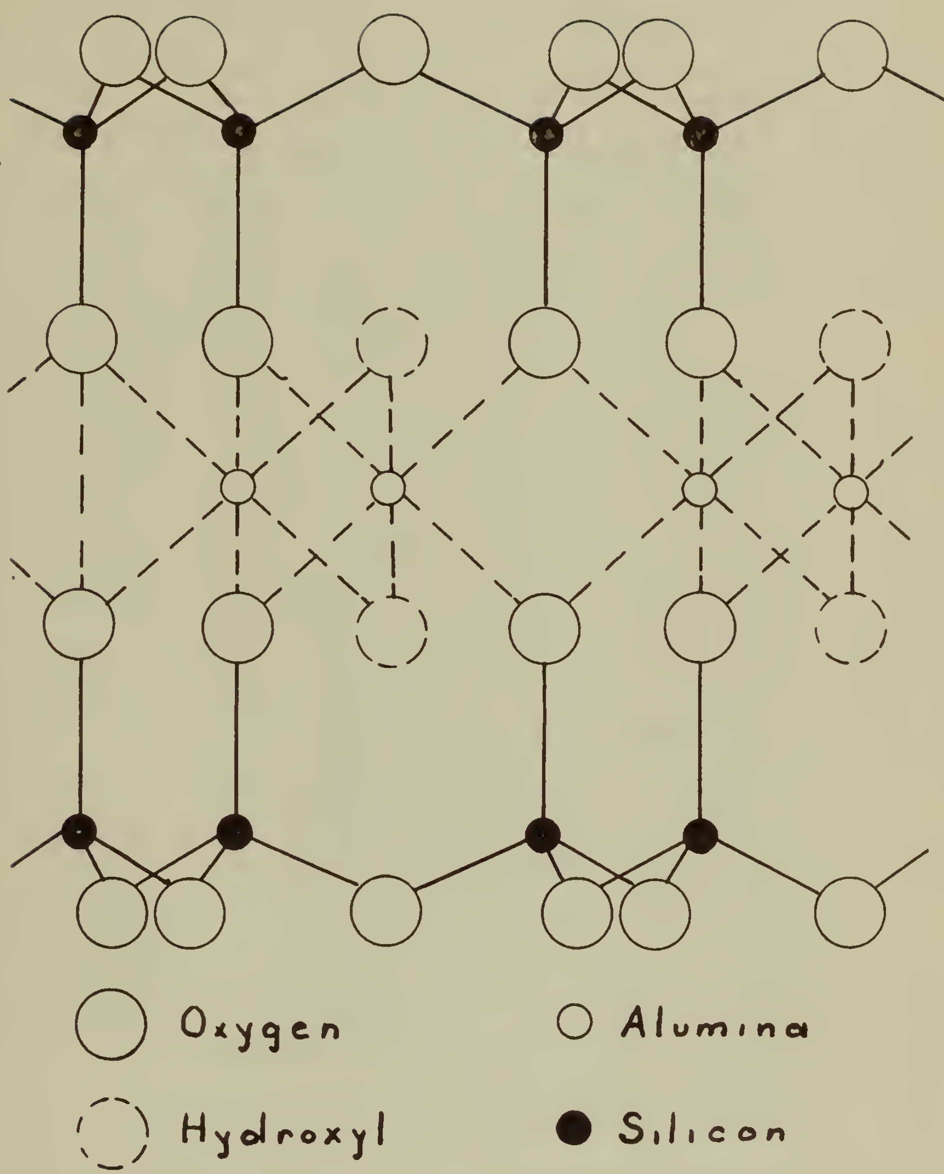


FIGURE II(b)

"Illite, Montmorillonite Space Lattice"

production. A very early type tube is shown by Figure III for the purposes of explanation. The tube is evacuated as thoroughly as possible to eliminate obstruction of the electron flow, and the filament, usually a tungsten wire, is heated by electrical current to incandescence. A potential gradient applied between the cathode and the target then draws the thermal electrons across the tube to the target where they impinge and produce x-radiation.

Present day tubes are much more simple and effective than the hot-cathode tube described above. It is now possible to increase the x-ray intensity, provide a variety of wave lengths, and perform many other desirable operations with the x-ray tubes. The tube used in accomplishing the diffraction work for this thesis is of the hot-cathode type and will be described under apparatus in Part II.

The x-rays produced by impingement of electrons on matter derive their energy from the original beam. Structural electrons in the atom are said to scatter the original beam. The scattered waves from several electrons in an atom combine so that the scattering effect from an atom is essentially a point source of scattered x-rays. Thus the atom will be considered as a point scattering source in explaining the geometry of diffraction.

C. X-ray Diffraction

With the impinging of a point source of x-rays on matter, several effects result: a portion of the beam may

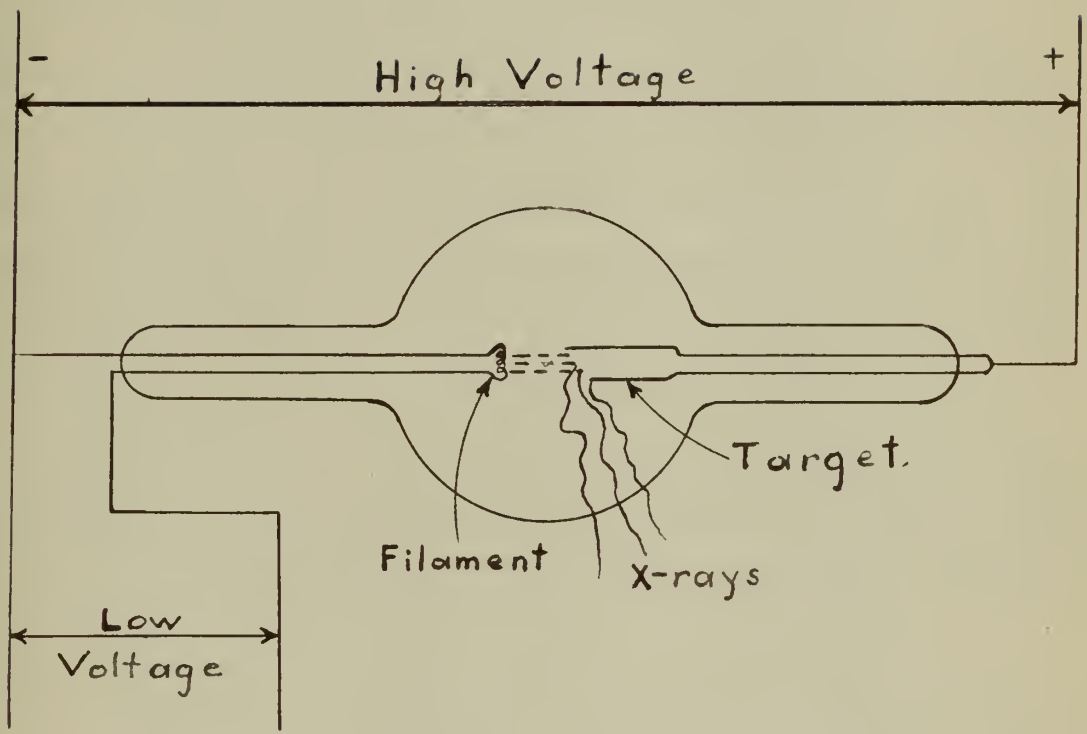


FIGURE III

"Early Hot-cathode X-ray Tube"

penetrate with reduction of intensity as energy is lost; electrons in the matter may be set into motion of frequency equal to the x-rays; free or loosely bound electrons may be struck, changing the wave lengths of the x-rays; or, if the x-rays are of sufficient energy, electons may be ejected from the target material. Diffraction occurs when an x-ray beam encounters a row of regularly spaced atoms. The atoms produce parallel wave fronts of spherically scattered waves of the same frequency and wave length of the incident beam. The direction of the common tangent to any succession of spherical wave fronts constitutes the wave front of a wave resulting from reinforcement of the scattered waves. Such constructive combination of the scattered waves is diffraction.

The formulation and explanation of diffraction has been simplified by Bragg's[2] analogy with the reflection of ordinary light from a mirrored surface. He considered that the array of atoms within a crystal forms a series of parallel lattice planes, the normal distance between them being noted by the symbol "d" (See Figure IV). The reflected ray from one plane will interfere constructively or destructively with the reflected rays from other planes. If the conditions are so arranged that the rays cause reinforcement, rather than destruction, then the lines of Figure IV, AB, A' B', are trains of incident x-rays of wave length λ impinging upon planes P, P_1 and reflecting off in direction B'C.

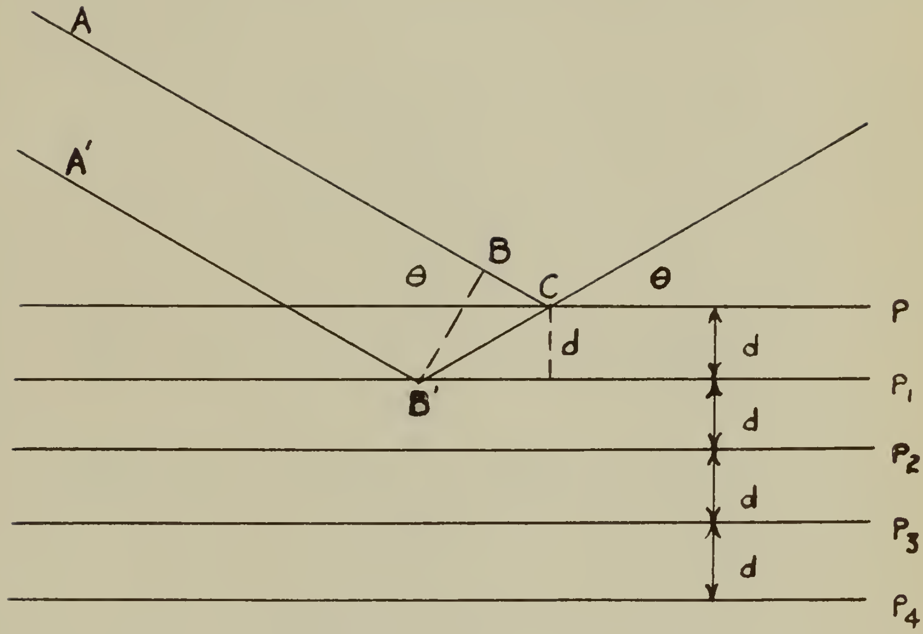


FIGURE IV

"Geometry of the Bragg Reflection Analogy"

The reflected wave B' must arrive at C in phase with wave ABC in order for it to reinforce the wave from C. This will be the case if the path difference is a whole number of wave lengths, that is, if:

$$B'C - BC = n\lambda$$

then

$$B'C = d/\sin\theta$$

and

$$BC = B'C\ \cos 2\theta = d(\cos 2\theta)/\sin\theta$$

then

$$\frac{d}{\sin\theta}(1 - \cos 2\theta) = \frac{d}{\sin\theta}(2\sin\theta) = n\lambda$$

and

$$\underline{n\lambda = 2\,d\,\sin\theta}$$

n = order of diffraction

λ = wave length of the incident radiation

d = interplanar spacing

θ = diffraction angle.

The above is known as the Bragg equation or law and is the fundamental formula of diffraction geometry.

Applied to the clay minerals, it has been previously explained that the minerals are made up of definite space lattices which vary in spacing with mineral type. A characteristic diffraction pattern for each mineral can be obtained corresponding to the specific spacing. In addition, the location and type of atoms within the various lattice planes cause the intensity of the diffraction lines to vary. This behavior

is also characteristic of the particular clay mineral studied.

D. Spectrometric Powder Technique

In the work of H. B. Keene[7] in 1913, the technique of crystalline analysis of powders was developed. The essential feature of this technique was an application of Bragg's law in allowing a narrow beam of x-rays to impinge upon a crystalline powder composed of fine, randomly oriented particles. Using Bragg's theory, it can be seen that all diffracted rays from sets of planes within the crystals will generate a cone of reflection of angle 2θ. By random orientation of the crystals, a fingerprint of the material may be obtained which will represent the diffracted rays from all available planes of the specimen. Several methods have been developed for x-ray analysis of powder samples. The best known is the Debye-Scherrer technique, but various specialized techniques such as symmetrical focusing method have also been employed extensively. Minor variations of the major techniques may involve rotating specimens, monochromatic radiation, and high or low temperature diffraction work.

The method used in this thesis is the spectrometric powder technique. This technique is not a new one and was applied as early as 1913 by the Braggs[8] when they used an ionization spectrometer to indicate the diffracted radiation from single crystals. The term "x-ray spectrometer" has been applied to the instruments which disperse x-rays of a single

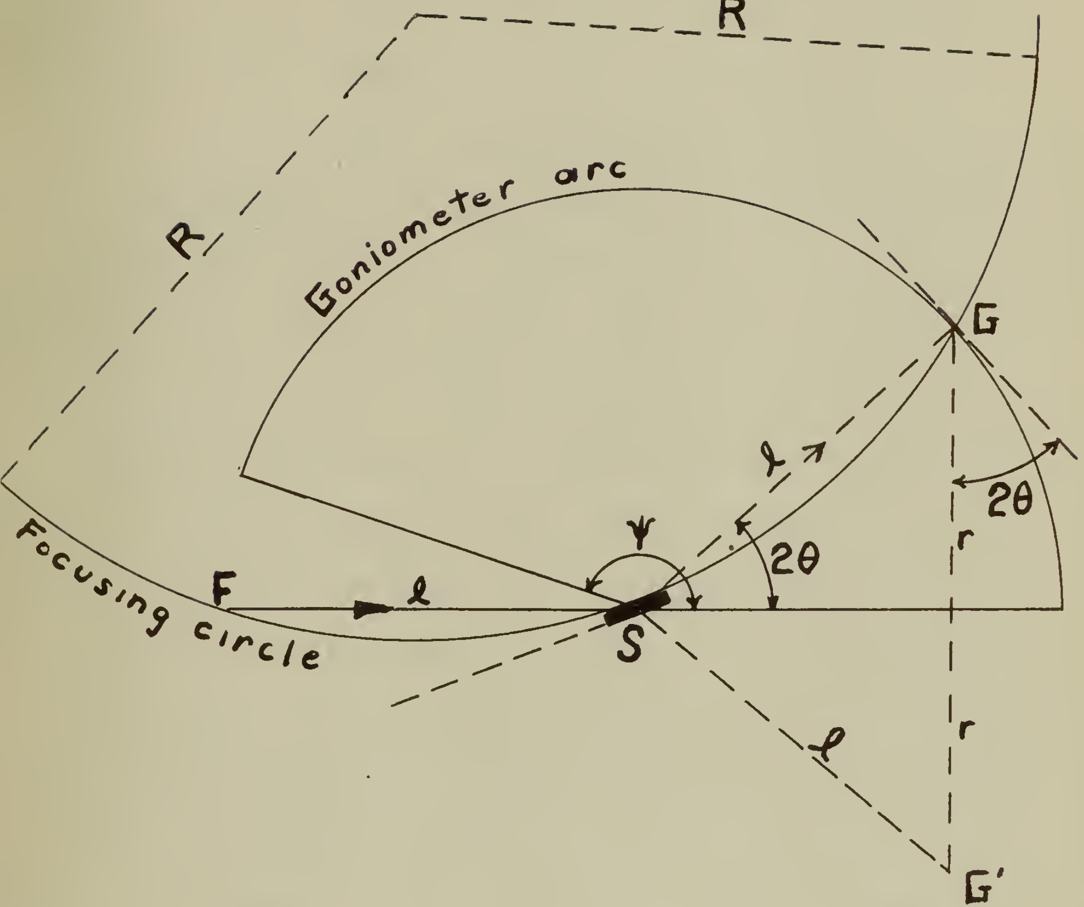


FIGURE V

"Geometry of X-ray Spectrometer"

wave length by diffracting them from planes of different spacings originating in fine crystalline powders. These instruments utilize a receiver (generally a Geiger-Mueller counter) for measurement of diffraction intensity at any particular (2θ) angle.

The geometry of the spectrometer is shown in Figure V. The sample is represented by S and consists of a fine powder contained in a suitable holder. The x-ray source is depicted as coming from F. The diffracted ray is then sent along λ to point G which represents the Geiger counter. The sample holder rotates as the counter traverses the goniometer arc, with the sample holder radius shown as R. It can be seen that the location of the Geiger counter on the goniometer arc bears a direct relationship to the (2θ) angle from the sample. This is the θ represented by the Bragg equation $n = 2d \sin \theta$, and it is possible with this equation to calculate the d spacing for any diffracted ray that is indicated by the Geiger counter. The intensity of diffracted rays picked-up by the Geiger counter is then automatically recorded by a scaler and a Brown recorder (described under Part III). The recorder plots (2θ) angles against intensity on a chart while the Geiger counter moves at a predetermined rate of speed over the goniometer arc. Where the intensities are reinforced by spherical waves from the sample, characteristic of the particular type material, the chart shows peaks above the background radiation being emitted.

The intensity of a given diffraction line or peak is dependent upon the following factors:

1. Intensity of incident beam.
2. Wave length of x-rays.
3. Crystal size.
4. Crystal perfection.
5. Mass absorption coefficient of the material.
6. Bragg angle.
7. Geometry involved in recording the pattern.
8. Scattering power of atoms of the material.
9. Temperature.
10. Electron diversity distribution.

As previously indicated, x-ray diffraction has become a powerful analytical tool in investigating the clay minerals. Exact lattice spacings can be determined leading to qualitative analysis, and, by measuring peak intensities, a semi-quantitative analysis is obtained.

E. Qualitative Analysis

It is possible to identify polycrystalline materials by application of powder diffraction techniques. Evaluation of this is one of the main objectives of this thesis as applied to clay minerals. A step-by-step procedure for clay mineral analysis is presented herein as Appendix D.

By using powder diffraction techniques, the following observations are possible:

1. The pattern obtained from the automatic record-

er is characteristic of the substance.

2. Each substance in a mixture produces a pattern independently of the others.

3. It is possible to tell the state of chemical combination of the elements in the material.

As explained before, it is possible to obtain a diffraction chart for an unknown material or combination of materials and then procede with a qualitative analysis. The first step is to compute the d or lattice spacing for each recognizable peak on the strip chart. This is accomplished by using the Bragg equation knowing the 2θ value corresponding to each peak.

Basic identification work was accomplished by Hanawalt, Rinn, and Frevel[9] wherein they compiled reference test data for many chemical compounds. Their compilation has been enlarged considerably and presently a complete American Society of Testing Materials Diffraction Data Card-file and Reference Book[10] is available for identifying unknown materials. This reference data includes most of the important clay minerals.

Having obtained the series of d spacings for an unknown compound, it is then possible to group these values in decreasing order of magnitude and then divide them into groups. This grouping is a scheme, established by Hannawalt, whereby the major groups[10] of compounds have been set-up. The ASTM reference cards are also grouped in accordance with

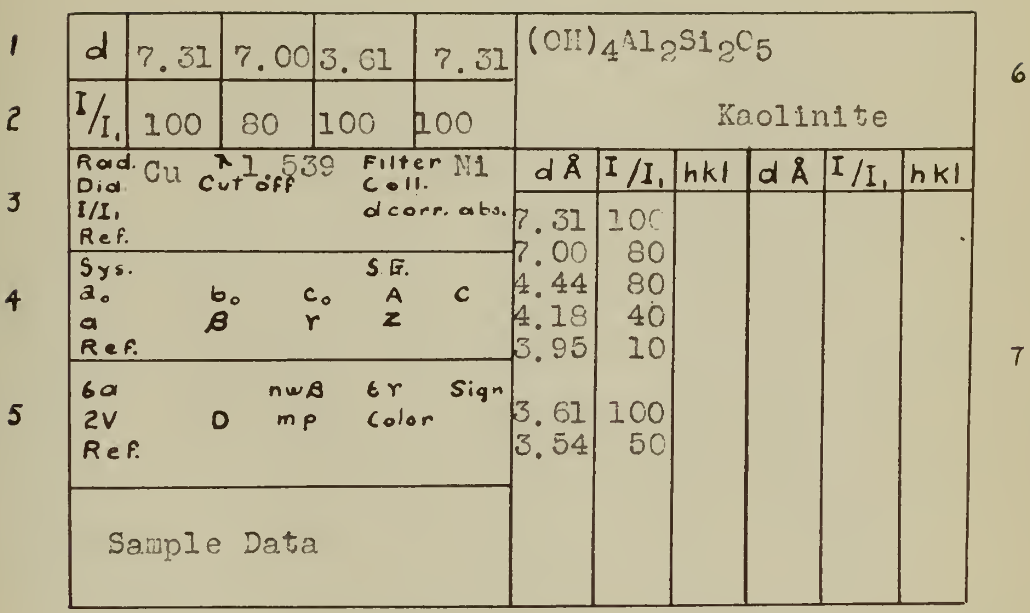
the Hannawalt scheme, and it is possible to compare unknowns to the standard cards and, ultimately, identify components of the unknown. The ASTM cards also list the relative peak intensities for each d spacing as further assistance in identification. A sample ASTM card is shown by Figure VI.

Due to the fact that each individual substance in a mixture has a particular set of d spacings, it is possible qualitatively to analyze the components of a given unknown from a single spectrometer chart.

F. Quantitative Analysis

Having identified a given material as described above, the next question is usually how much of it is present. An answer is possible due to the fact that a nearly linear relationship exists between concentration of material and the observed intensity of its spectral peaks. On this basis, a calibration curve can be plotted for a known standard material by varying the concentration of the standard by weight and observing the resultant peak intensity above background from the diffraction strip chart. The intensity, in such a case, is best determined by integrating the area under the peak on the spectrometer trace using the extrapolated background as a base line. Integration may be conveniently carried out with a polar planimeter. Such a procedure was previously used for clay minerals by R. D. Blotter[11] with good results.

As an extension of Blotter's investigation, this



1 - Interplanar spacings
2 - Line Intensities
3 - Experimental Data
4 - Crystallographic Data
5 - Optical Data
6 - Chemical analysis
7 - Tabulation of d spacings and intensities

FIGURE VI

"ASTM Diffraction Data Card"

thesis is concerned with quantitative analysis of clay minerals by use of an internal standard. It was known that a calibration curve could be prepared by proportioning gravimetrically an internal standard with a clay mineral and then either calculating the area of the resulting peak intensities of the two materials and plotting as a ratio; or, as was done, measuring the relative height of the two peaks which, when plotted against the ratio of weights for a series of mixtures, produces a straight-line curve as obtained in Appendixes A through C. The method of choosing the internal standard and the proper peaks to be used will be explained in Part IV.

Once a calibration curve is obtained, it is possible to add the internal standard to the unknown quantity of the sample being tested and obtain a ratio of the clay mineral peak height to the internal standard peak height. Using this ratio, reference can then be made to the calibration curve for the actual quantity of unknown present.

Calibration curves have been prepared for the three main clay mineral types using the internal standard technique. The results are included under Appendixes A, B, and C.

PART III.

APPARATUS

A. Sample Preparation Apparatus

Three major items of equipment were utilized in preparation of the clay mineral samples for x-ray diffraction. They are: (1) the CENCO-MEINZER sieve shaker, (2) the DUMORE high-speed mechanical stirring apparatus, (3) the INTERNATIONAL, size 1, type C centrifuge. The actual procedures and reasons for the use of this equipment are contained in Part IV and only the description is presented here.

1. The CENCO-MEINZER Mechanical Shaker is simply a spring mounted, motor operated platform used for separation of powdered materials into various components by mounting sieves on the platform and shaking for approximately five minutes. Three sieves were used: a 40 mesh sieve, a 200 mesh sieve, and a 325 mesh sieve in series. A collection container was placed below the 325 mesh sieve from which the final powders were obtained.

2. The DUMORE high-speed mechanical stirring apparatus was used to achieve dispersion and ionic saturation of the sample. Figure VII (a) shows the apparatus with its component parts. The parts are the stand, a mixing container with detachable baffils, and a type 6 M, 115 volt, high-speed motor which provides stirring up to speeds of 15,000 rpm.

3. The INTERNATIONAL centrifuge is operated by a 1/8 HP AC motor at speeds from 1,800 to 3,000 rpm. Centri-

fugal force is generated equal to 500 to 1,780 times gravity by varying a control rheostat. After the samples had been ionically saturated, they were centrifuged, at a rheostat setting of 15, in this machine. Figure VII (b) is a photograph of the centrifuge.

B. <u>X-ray Diffraction and Recording Apparatus</u>

The apparatus used in performing the x-ray diffraction of the clay minerals consisted of the following major items:

1. <u>X-ray tube</u>. A Norelco four-window x-ray diffraction tube was used. This tube permits use of three powder cameras and one goniometer, simultaneously, by providing a high intensity radiation source with four ports. In this case, however, only one port was needed - that for the goniometer. The other three ports were kept closed at all times.

Many types of x-ray tubes are available for diffraction work ranging from targets providing short wave lengths, such as molybdenum, to the longer wave lengths of chromium. For use with clay minerals, a copper target x-ray tube was chosen to give x-radiation of approximately the lattice spacing of the minerals and, therefore, better diffraction data.

The copper tube provides x-radiation of 1.542 Å wave length. It is a hot-cathode type tube and is a modification of the tube shown in Figure III. A sealed evacuated glass tube containing two electrodes makes up the main part.

(a)

"Dumore High-Speed Stirring Apparatus"

(b)

"International Centrifuge"

FIGURE VII

The cathode is a spiral of tungsten wire and is heated to incandescence by passing a current through it. Electrons emitted from the hot filament are focused into a narrow beam by a metal cup. This beam strikes the copper anode or target at a high velocity. A small portion of energy of the high-speed electrons is converted to x-rays, and the balance converted to heat energy. Due to the large percentage of heat energy generated, a cooling system is provided that surrounds the tube with circulating water at all times. Stoppage of this cooling water during operation will ruin the x-ray tube; therefore, a mercury contact safety switch and a pressure switch are incorporated into the power and water supply to automatically cut off the filament current for the tube if cooling water is not maintained.

A Coolidge step-down filament transformer provides the current for heating the tungsten filament. A rheostat in the primary circuit of the transformer controls the current through the filament and, in turn, the current through the x-ray tube. Panel settings for the copper target tube are 70 KV with 15 Ma.

2. High-angle, precision, Geiger-counter goniometer. The goniometer consists of a frame (mounted on the same table supporting the x-ray tube), drive motor, angular vernier, specimen holder, and a Geiger-Mueller tube. Figure VIII shows a breakdown of the parts that are exposed. One of the three camera ports is indicated along with the port

used for the Geiger-Mueller counter.

The specimen holder shown is so arranged that a 1:2 ratio of rotational speed is maintained between it and the Geiger tube. This satisfies the geometry of the Bragg equation, as depicted by Figure V, at all times during the travel of the Geiger tube through its arc. The angle of (2Θ), also shown by Figure V, is automatically registered by a Brown automatic recorder which will be discussed later. The speed of travel of the Geiger tube can be controlled by a simple choice of gears, and for this thesis a speed of 1^{o}2Θ per minute was used.

The Geiger-Mueller tube, marked on Figure VIII, travels through a possible arc from -9^{o} to 163^{o}(2Θ). Its geometric location is indicated on Figure V as point G with its travel range shown. The Geiger-Mueller tube, itself, consists of a sealed outer glass envelope containing a central wire which, in turn, is surrounded by a grounded co-axial cylinder. The tube is filled with a gas mixture consisting of argon and oxygen. A high positive potential is maintained between the central wire and its surrounding tube. As quanta (diffracted x-radiation, in this case) of sufficient energy strikes the gas molecules in the tube, they eject photoelectrons which are drawn toward the center wire by the high potential. A process of successive ionization takes place in the tube, and the result is an accumulation of electrons around the central wire. This accumulation occurs in

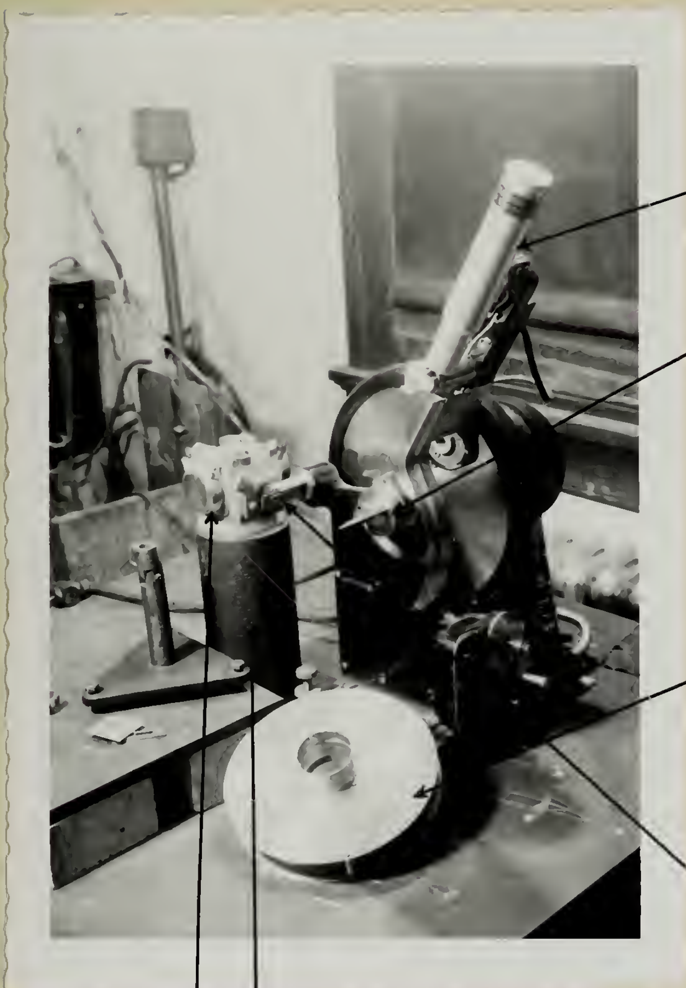


FIGURE VIII

"NORELCO High Angle Goniometer"

a very short time, in the order of a few microseconds, and produces an electrical impulse which is transmitted from the central wire to a photomultiplier unit and then to a scaling circuit and a recorder.

Several types of slits are used between the line of the x-ray tube and the Geiger counter including: divergence, receiving, and scatter slits. The divergence and receiving slits collimate the x-ray beam produced by the x-ray tube and the diffracted rays respectively, and provide a better source without substantial loss of intensity. The scatter slit also collimates the beam and cuts out scattered x-rays allowing only those diffracted from the specimen into the receiver. This action materially cuts down the amount of background received. The manufacturer has available slits for various ranges of the goniometer and those used were as follows:

1° slits - (18° - 76° 2θ)

$\frac{1}{2}^\circ$ slits - (9° - 18° 2θ)

$\frac{1}{4}^\circ$ slits - (4.5°- 9° 2θ)

3. In addition to the previously described equipment, the unit included an electronic circuit panel shown in Figure IX, a scaler counter, an amplifier unit, a Brown Recording Potentiometer, and a high voltage supply.

The pulses produced from the Geiger counter, explained previously, are amplified and sharpened by the amplifier unit. They are then fed into a pulse-averaging

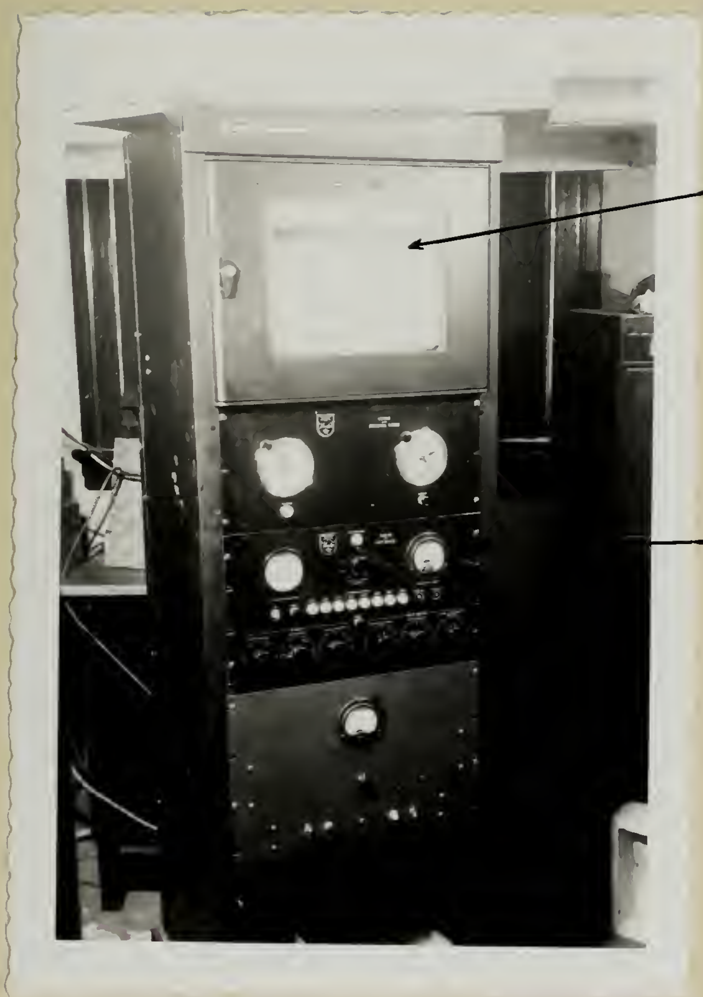


FIGURE IX

"Electronic Circuit Panel and Recorder"

circuit which smooths out the pulses and sends them to the scaling circuit which, in turn, counts them. The scaler-counter is necessary since a mechanical counter is unable to count the pulses fast enough. Therefore, they are scaled down before feeding to the mechanical recorder. The mechanical recorder produces a strip chart showing diffraction peaks at definite (2θ) angles for the range of Geiger tube travel.

PART IV.

METHOD OF PROCEDURE

A. Sample Preparation

1. Samples. In order to procede with the analysis of an unknown clay mineral, it was first necessary to establish that calibration curves could be plotted by the use of standard clay mineral samples by applying an x-ray diffraction technique. The standards used were obtained through Wards Natural Science Establishment, Inc., and included standards of the three major clay minerals: a Mesa Alta, New Mexico, Kaolinite; a Morris, Illinois, Illite; and a Otay, California, Montmorillonite. The chemical analysis of these standards is contained in the API Handbook,[12] and they are approximately 90% pure mineral.

2. Unknown clay sample. The unknown clay sample used herein was obtained from the St. Lawrence Seaway Project through the Department of Soil Mechanics of the State of New York. Two samples were received, each from a different elevation of the seaway route. The samples were a dark, clay-like material and were very wet in their original condition.

3. Sample preparation. The standard clay minerals obtained were first sized to a powder by grinding or filing from the original mass until the resultant powder could pass a screening through a 200 mesh sieve. At this point, the powder was worked with a mortar and pestle in order to obtain

a size powder that would pass a 325 mesh sieve. The 325 mesh powder size is recommended for x-ray diffraction use by Klug and Alexander[10] and the results of using such a size will be explained under Part V.

With the samples sized as desired, the next step was the ionic saturation and elimination of organic matter from each. Previous analysis of clay minerals have shown that they occur in nature with four main cations, namely: Hydrogen (H^+), Sodium (Na^+), Potassium (K^+), and Calcium (Ca^{++}), and that each of these absorbed ions cause different clay action to take place. Cations influence swelling, dispersion, flocculation, plasticity, viscosity, permeability, etc., in clay mineral action; consequently, it can be seen that for proper calibration curves to be used for identification of clay minerals, it is important that the sample be of a known ionic saturation such as Kaolinite (K^+), Illite (H^+). In addition to ionic saturation, organic matter also influences clay minerals. It was necessary, therefore, to remove all of this material possible.

The method used to accomplish the above is outlined by Baver[5] and was taken from an adopted method of the International Society of Soil Science for soils. The procedure is as follows:

a) Removal of organic matter. A 16 gram sample of the clay mineral was oxidized in 30 cc of 6 per cent solution of H_2O_2 by boiling for 5 minutes.

b) The sample was then centrifuged for 10 minutes in the International Centrifuge and the supernate was poured off.

c) The residue was treated by stirring in the Dumore High-speed Stirring apparatus with 20 cc of 0.17N Hydrochloric Acid for a period of 1 minute. Again the mixture was centrifuged and the supernate poured off. This provided a removal of the carbonates.

d) The residue was then washed with distilled water three times for removal of any contaminating matter. This included three successive centrifugings.

e) The above procedure provided a Hydrogen (H^+) ion saturated clay. It was then necessary to quarter the sample, retaining one quarter as (H^+) clay and to peptize the other three with solutions of 0.008N Sodium Hydroxide, Calcium Hydroxide and Potassium Hydroxide. This was accomplished by mixing the quarters with the desired solutions for 20 minutes in the Dumore mixer and then centrifuging as before.

f) The four samples were then dried in a furnace at a temperature of 110°C for at least 3 hours.

g) The final step was to again work the dry sample by mortar and pestle until it could pass a 325

mesh sieve.

The unknown sample was dried and then prepared as described above except that step (e) was excluded for reasons that will be explained under Part V.

4. Sample Mixing. As explained in Part I, the internal standard technique of x-ray analysis provides a means of comparing a known standard to an unknown and thereby, with the use of calibration curves, ascertaining the quantity of the unknown in a mixture. This is possible by comparing the relative peak intensities from a diffraction strip chart of the unknown and the internal standard.

Important considerations in the choice of an internal standard are that it be pure, of a suitable crystalline size to give sharp diffraction lines, and that it provide strong diffraction lines near but not overlapping the lines of the unknown.

In addition to the internal standard, it is possible to add a diluent to the sample mixture used in preparation of calibration curves and obtain a percentage value of the unknown from the resultant curve (see Appendixes A, B, and C).

After many trials of materials listed in the ASTM X-ray Diffraction Data Book[13], the best standard for Kaolinite and Illite was found to be Mercurous Chloride (Hg_2Cl_2) and for Montmorillonite was Zinc Sulfite ($Zn(S_2O_4)$. In both instances, Calcium Carbonate ($CaCo_3$) was found to provide a

diluent with no peak interference with either the clay minerals or the standards. Both standard and diluent were powders of a particle size less than 325 mesh.

A series of four mixes proportioned gravimetrically was prepared to give a range from 100 per cent to zero amount of clay mineral. The actual mixes used for each type clay mineral are contained in Appendixes A, B, and C.

Mixing was accomplished by placing the components in a 7 dram plastic bottle and rotating end over end for one hour minimum time on the shaft of a slow speed electric motor. To aid the mixing, several small glass balls were also added. The time of mixing was determined by trial in running samples at different mixing times and comparing peak intensities until a maximum peak was obtained.

5. Sample Mounting. The sample holder for the x-ray spectrometer provided by the manufacturer is an aluminum flat plate with a 3/4 by 3/8 inch rectangular hole in the upper half as shown by Figure X (a). The holder is $1\frac{1}{2}$ by 1 3/8 by 1/16 inches and has an alignment groove down the center. The rectangular hole is for the sample mounting.

The amount of sample necessary to fill the hole is somewhat less than 0.5 grams. It was found that the clay mixtures could be mixed and handled better in 3 grams quantities, therefore, there was considerable excess with each sample.

Actual mounting of the sample in the holder can be

accomplished in several ways, the easiest and fastest is as follows:

a) The sample holder is laid face down on a piece of glass. The sample is then poured into the hole in sufficient quantity to more than fill the hole.

b) The material is then tamped with the end of a small spatula to insure that all corners are filled. The spatula is then used to press the powder firmly into the holder.

c) The excess is cut off flush with the back of the holder with a razor blade. A glass slide, exactly the size of the holder, is placed on the back as shown in Figure X (b).

d) The whole unit (glass back, holder, and original glass in front) is turned over, and the front glass removed leaving only the holder and glass slide as shown in Figure X (c). The two may now be Scotch-taped together keeping the tape away from the sample rectangle.

The mounted sample is now ready to be placed into the spectrometer clip or covered and set aside for future use.

6. Sample Exposure. A preliminary determination strip chart run for Kaolinite and Illite revealed the I_{100} or highest intensity peak for each. After this was established, and the internal standard chosen, it was necessary to run the samples only through the range that covered the two peaks

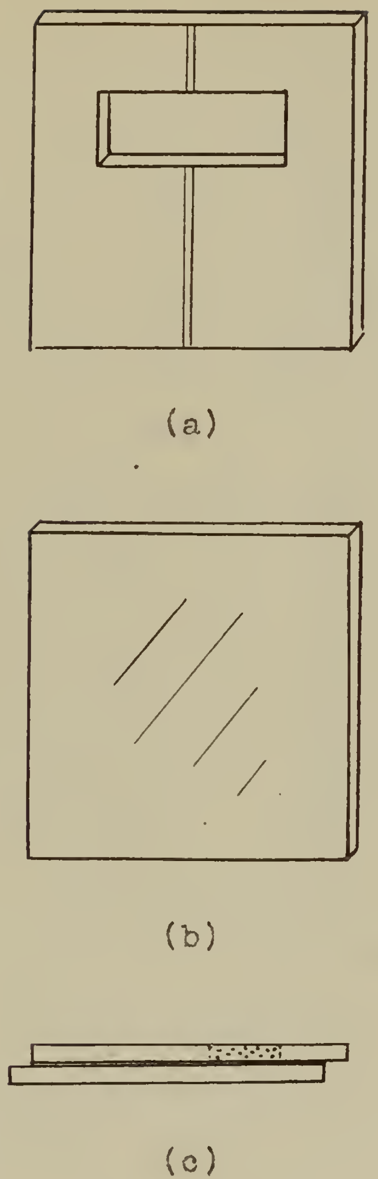


FIGURE X

"Goniometer Specimen Holder"

to be used in plotting the calibration curves. In most cases, these were the I_{100} of the clay mineral and the I_{100} of the internal standard. For the Kaolinite - Mercurous Chloride mixture, the range was 23° to $30^{\circ}(2\theta)$ with peaks at d = 3.19 Å for Kaolinite and d = 3.60 Å for Mercurous Chloride as can be seen from Appendix A. The Illite - Mercurous Chloride mixture required a range of 26° to $31^{\circ}(2\theta)$ with the Illite I_{100} peak at d = 3.37 Å and the Mercurous Chloride identical to the above as shown by the strip chart of Appendix B.

The complete strip chart run for Montmorillonite in the range 0° to $70^{\circ}(2\theta)$ revealed that the I_{100} peak falls at an (2θ) angle of $4.5^{\circ}(2\theta)$. At or near this point, there is also an intense diffraction peak which is an inherent feature of the spectrometer used. Because of this, the I_{100} Montmorillonite peak could not be used for analysis. Therefore, inspection of the complete range $(0 - 70^{\circ} 2\theta)$ provided a peak of I_{80} or 20% less than the I_{100} in intensity at $19.6^{\circ}(2\theta)$ or a d spacing of 4.52 Å. Since it is immaterial which peaks of the internal standard and the clay mineral are compared as long as the same peaks are used for the unknown sample consistently, the I_{80} peak of Montmorillonite was compared to the I_{100} peak of the internal standard (Zinc Sulfite in this case).

It can also be seen from the strip charts of Appendix C that a different scale factor was used for the two peaks. The Zinc Sulfite was run under a scale factor (SF) of

8 and a time constant (TC) of 4, while the Montmorillonite was under a scale factor (SF) of 4 and a time constant (TC) of 8. Again, the investigator must be consistant in the use of scale factors in order that the calibration curves may be valid. The angular range for the Zinc Sulfite was from 9° to $13^{\circ}(2\theta)$ and that of the Montmorillonite from 16° to $23^{\circ}(2\theta)$.

Appendixes A, B, and C include only one strip chart run for each mixture. Actually, each mixture was run three times, and the peak heights were averaged as can be seen in the Data Accumulation Tables of these same Appendixes. In the interest of brevity, the other strip charts were not included herein but are available in the x-ray diffraction file of the Department of Civil Engineering, Division of Soil Mechanics and Sanitary Engineering, Rensselaer Polytechnic Institute.

7. Interpretation of diffraction charts. The relative peak heights used in plotting the H_u/H_s points for the claibration curves of Appendixes A, B, and C were measured by first marking a line through the center of the background approaching the peak to the center of the background past the peak. The height was then measured to the apex of the peak from this line by use of a #20 engineer's scale. The relative heights were calculated and tabulated with the ratio of weights G_u/G_s in the tables at the end of the Appendixes. From this, the calibration curves were plotted.

PART V.

RESULTS, CONCLUSIONS, AND RECOMMENDATIONS

A. Results

The results of the experimental investigation used in working toward the goal stated in Part I (B) are included as Appendixes A through E.

As stated in Part I, the specific goal of this thesis was: (1) to establish califration curves for standard clay minerals using the internal standard technique; (2) to establish a step-by-step procedure for qualitative and quantitative analysis of clay compounds; (3) the actual application of (1) and (2) by trial using an unknown. The following is a description of the results leading toward these goals:

1. Calibration curves obtained by x-ray diffraction analysis of a mixture of the pertinent clay mineral, a suitable internal standard, and a diluent have been established for the following clay minerals: Kaolinite (Appendix A), Illite (Appendix B), and Montmorillonite (Appendix C). These curves show the possibilities of such a procedure in the quantitative analysis of a clay mixture. It is possible, with a calibration curve, to ascertain the quantity of clay mineral in a mixture by using an internal standard. An excellant approximation of the clay mineral content can be obtained by comparing the relative peak intensity ratio of the internal standard and clay mineral (H_c/H_s) to the known weight of the standard. This follows from the linear behav-

ior of the H_c/H_s ratio as a function of the G_c/G_s ratio.

Deviations from a linear relationship of the points shown by the calibration curves of Appendixes A, B, and C are results of errors in the diffraction system and are explained herein under Conclusions.

It was possible to plot per cent of clay mineral on the calibration curve by using a diluent in the mixtures. This allows the investigator to obtain a percentage immediately from the curves by using relative peak intensities from diffraction charts.

2. The procedure for investigating clay compounds set forth in Appendix D is a result of the work undertaken in plotting the calibration curves. By actual practice, it was possible to list suggested steps that will enable future investigators to analyze clays without extraneous work. Many of the steps used in this investigation were found to be unnecessary and are not included in this thesis. Likewise, some methods are thought to be better than those previously employed, and are included. Reasons for using or excluding certain procedures are also contained herein under Conclusions.

3. Application of the resulting procedure of (2) above led to the report of Appendix E. This report is as thorough as was possible with the limited preparation time available and gives a fairly concise picture of the qualitative and quantitative analysis possible for an unknown

such as the clay compound of Appendix E which was taken from the subsoil of the St. Lawrence Seaway Project. It should be noted, whenever possible, that such an analysis should be supplemented by other methods of analysis such as chemical, differential-thermal, particle size, Atterberg limits, etc. Thus the x-ray evidence can be corroborated by different lines of approach. However, x-ray diffraction analysis, such as is contained in Appendix E, does give basic information on the clay mineral and directs the researcher to the additional analyses necessary for complete investigation.

B. Conclusions

The main conclusion reached by this research is that the internal standard technique used in analysis of clay mineral compounds provides an excellent tool for clay mineral research. As an example, the quantitative analytical chemist can give the element composition of a material, but usually has great difficulty in distinguishing the chemical identity of the various phases of a mixture and in determining the precise amounts of each phase present. The use of this analysis with a known internal standard, as was done herein, provides a good quantitative procedure. The report of Appendix E verifies this conclusion and shows an application of the main features of this thesis.

In addition to the above, several conclusions had

to be reached in order to prepare the step-by-step procedure of Appendix D. These conclusions are outlined as follows:

1. Ionic saturation. It is believed that ionic saturation of an unknown clay mineral for qualitative and quantitative analysis is unnecessary unless the researcher is trying to obtain a very accurate and complete analysis. The variation of the calibration curves for the four saturation ions (K^+, Na^+, Ca^{++}, H^+) is negligible, and it is recommended that the unknown sample be treated only to remove organic matter as described in Part IV excluding step (e). By treating the mineral to remove organic matter, a mineral saturated with H^+ ion is obtained. Calibration curves can then be as accurate as is usually necessary.

2. Particle size. It is concluded that the particle size used should be as small or smaller than powders passing a 325 mesh sieve. In diffraction of powders of larger size, insufficient randomly oriented crystals are contained in the sample to yield a reproducible or true average intensity. Below a 325 mesh, the accuracy of peak height is greatly improved.

In addition, the finer the powder, the better the sample mounting that can be obtained. A powder passing a 200 mesh sieve was tried and could not be retained as well in the sample holder as the finer powder. Powders, passing a 325 mesh sieve, mounted in the holder, have sufficient affinity between particles, sides of the holder, and glass

backing so that the holder may be rotated through 180° without the sample falling out.

3. Specimen mounting. Mounting of the powder samples is much easier, faster, and better accomplished by using the glass backing as described in Part IV. A major concern in clay mineral analysis by x-ray diffraction, described previously, was in mounting the specimen (see Blotter[11]). The method described here, using fine powders, eliminates all trouble encountered in other methods and also reduces inaccuracies due to preferred orientation.

4. Sources of error. Attainment of high precision and reproducibility in intensity measurements demands careful attention to a number of major factors:

a) Crystallite size of powder - this consideration was mentioned above. Powder particle size should be smaller than that passing a 325 mesh screen. Preferred orientation of the powder crystallites reduces considerable the accuracy of peak intensities. As yet, there is no known way of completely eliminating preferred orientation, but small particle size will reduce its effects to a minor source of error.

b) Mixing of standard with the sample - improper mixing, of course, will reduce intensity accuracy since one component may predominate in the irradiated surface leading to disproportionate inten-

accuracy since one component may predominate in irradiated surface leading to disproportionate intensity values. Mixing by rotation for at least one hour, as described, gave reproduciable results.

c) Mounting of specimen - mounting procedures, outlined previously, tend to decrease the errors due to this factor. It is comparatively easy to attain a well-mounted sample of proper thickness using a glass backing. This method is especially preferable over the Ducco-cement system as it eliminates cracking and shrinkage of the specimen which may occur during drying.

d) Goniometer alignment - correct alignment of the goniometer is essential to attainment of maximum intensities and proper angular readings. The manufacturer's instructions for such alignment should be followed prior to any series of diffraction analyses. A check is readily available by running a standard powder material and by comparing the resulting strip charts with the manufacturer's standard strip charts that are included in the equipment manual.

There are other factors that contribute to error in spectrometer data, but it is possible to attain good results by following exactly the outlined procedure at all times. Errors are apparent in the calibration curves of Appendix A,

B, C, and E in that many points in the curves do not fall exactly in a straight line. None, however, are excessively in error, and it is believed that the use of these curves will give a good approximation of quantity in an unknown clay compound.

C. Recommendations

It is recommended that future clay mineral research work follow the procedures set forth in this thesis. It is recognized that improvement of the techniques are definitely possible with added study and research.

The following specific recommendations are made as proposed applications and improvements that can be attempted in this field:

1. The study of clay minerals can be improved greatly by the use of differential thermal and x-ray diffraction methods combined. According to P. Chiotti[14], it is possible to adapt a specimen holder and furnace for use as auxiliary equipment with the goniometer used for this thesis.

2. X-ray diffraction procedures can be applied to the actions of clay minerals under varied conditions to study the minerals' reactions. Suggestions are: (a) swelling of clays at various moisture contents; (b) fixation of space lattice by potassium ion saturation.

3. The use of a rotational specimen holder would improve the geometry of the goniometer and sample and thereby improve the intensity and location of diffraction peaks.

Such a holder can be purchased from the North American Phillips Company.

4. Investigations of the low angle range from 0° to $9^{\circ}(2\theta)$ would improve the qualitative analysis of the minerals, especially Montmorillonite. This involves purchase of additional divergence and scatter slits for use with copper x-radiation.

5. As a further step in analysis of clay minerals, it is suggested that research be accomplished using the electron microscope available in the Department of Physics and using the spectrographic equipment available in the Department of Metallurgy at Rensselaer Polytechnic Institute.

PART VI.

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APPENDIX A

Diffraction Strip Charts and
Calibration Curves for Kaolinite
with Internal Standard

Clay Mineral - Mesa Alta, New Mexico, Kaolinite

Internal Standard - Mercurous Chloride

Diluent - Calcium Carbonate

APPENDIX A

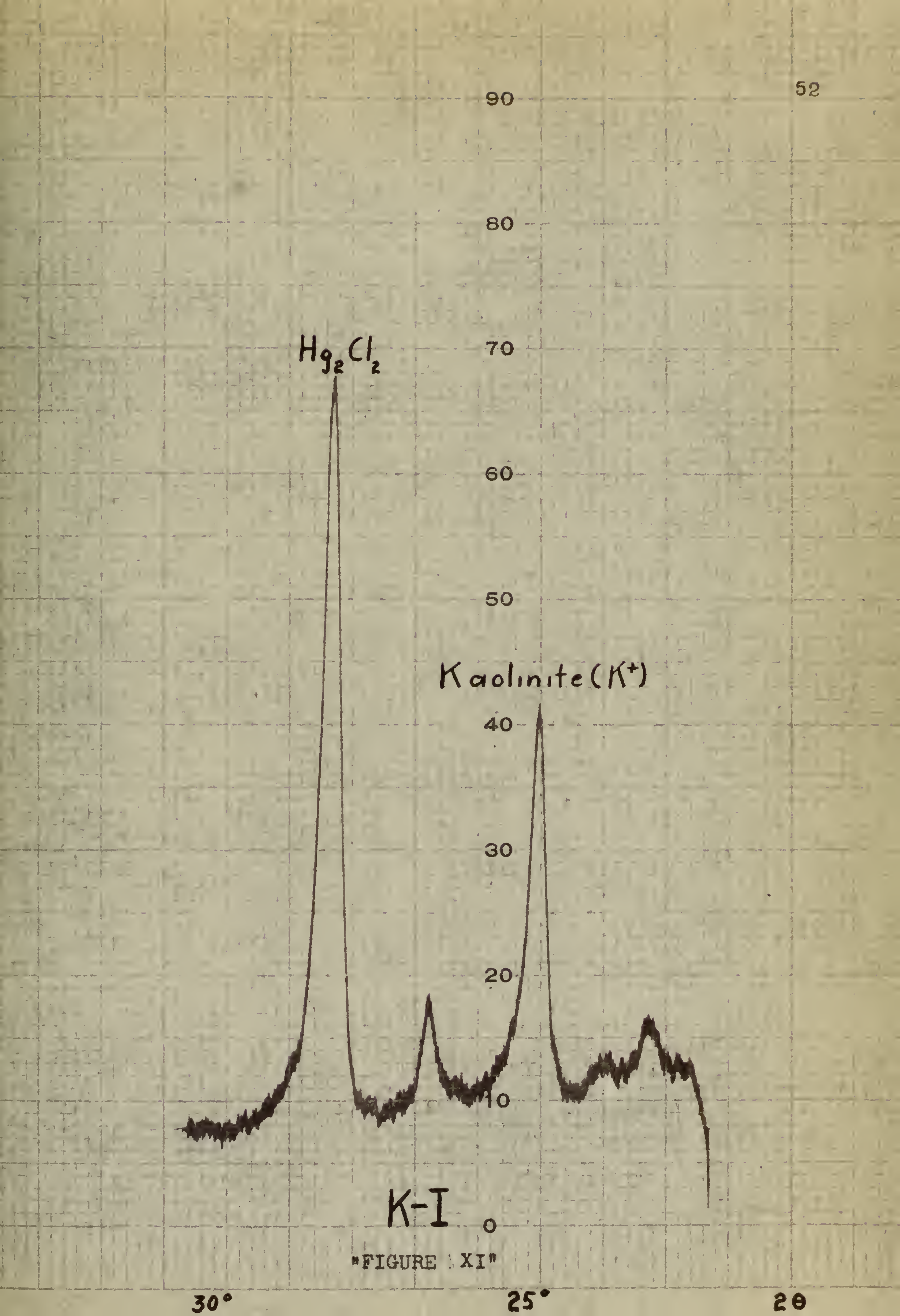
SECTION I

Ionic Saturation (K^+)

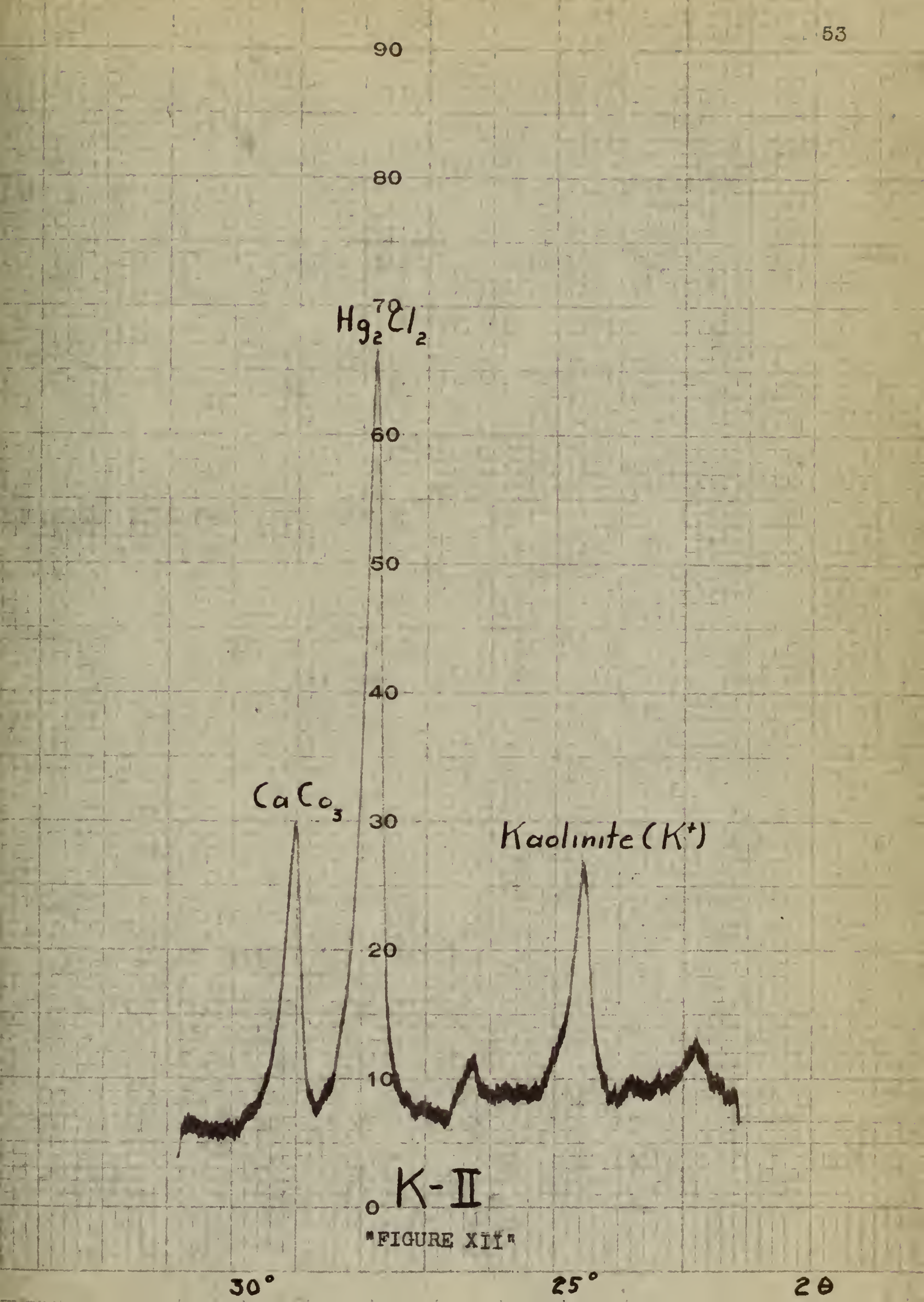
Mixtures:		Weight (grams)			
		K-I	K-II	K-III	K-IV
Clay Mineral	- Kaolinite (K^+)	2.00	1.40	0.80	0.40
Diluent	- $CaCo_3$	0.00	0.60	1.20	1.60
Standard	- Hg_2Cl_2	1.00	1.00	1.00	1.00

Spectrometer Data

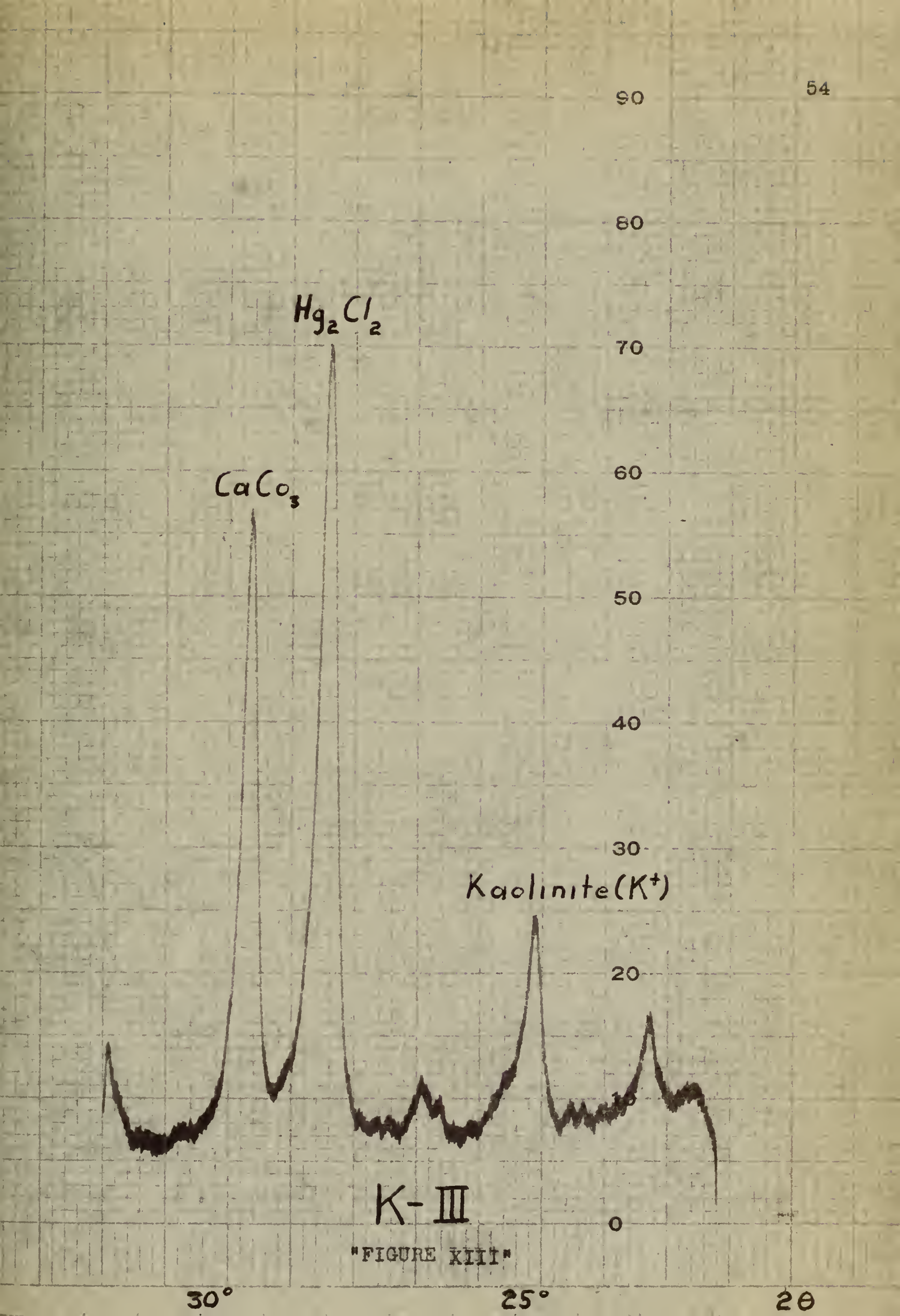
Radiation:	Copper
Filter:	Nickel
KVP:	70
Scanning Speed:	$1^o(2\theta)$/MIN
Rate Meter:	SF 8
	M 0.6
	TC 8



"FIGURE XI"

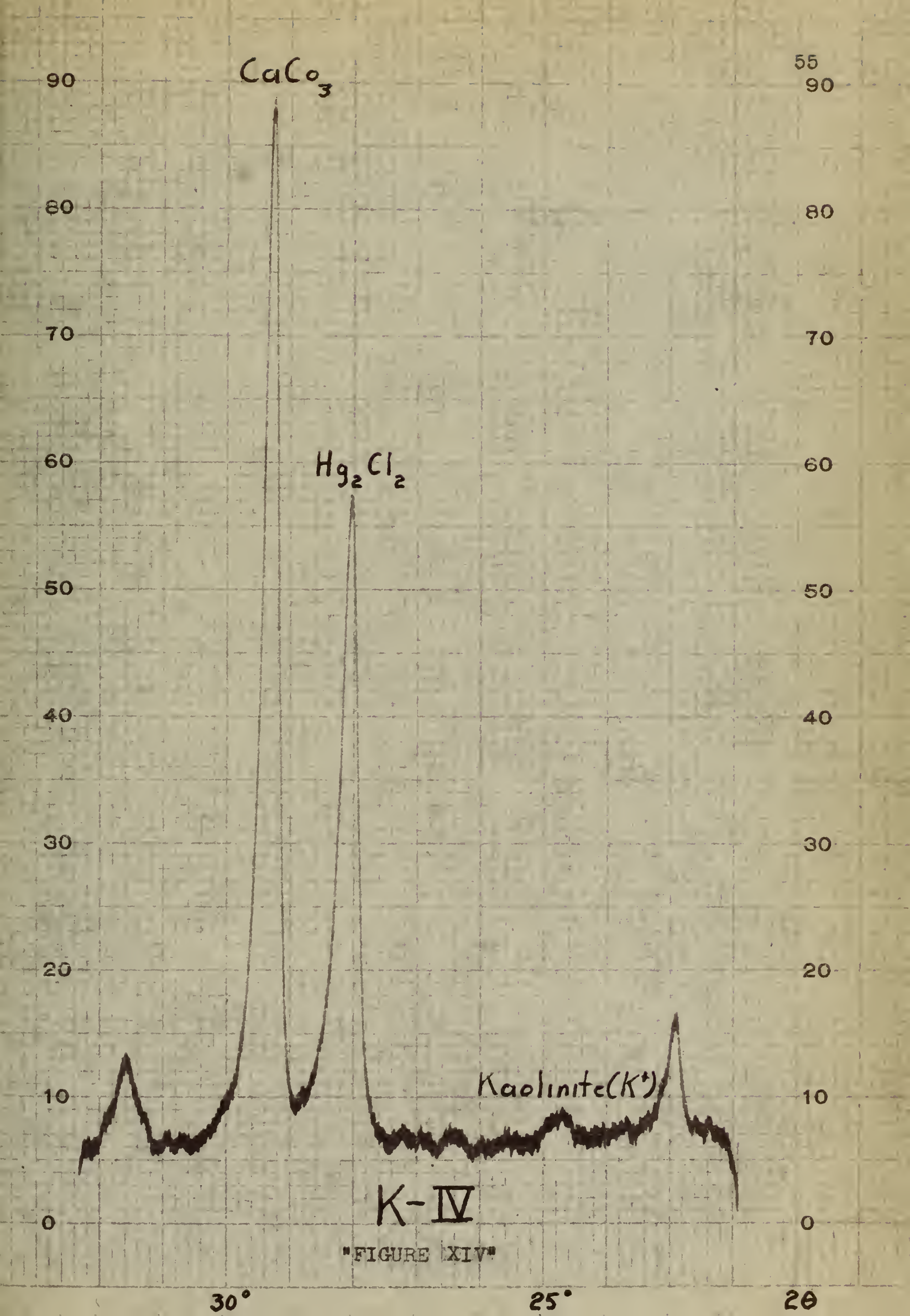


"FIGURE XII"



90
80
Hg_2Cl_2
70
$CaCo_3$
60
50
40
30
Kaolinite(K^+)
20
10
0
K-III
30°
25°
2θ

"FIGURE XIII"



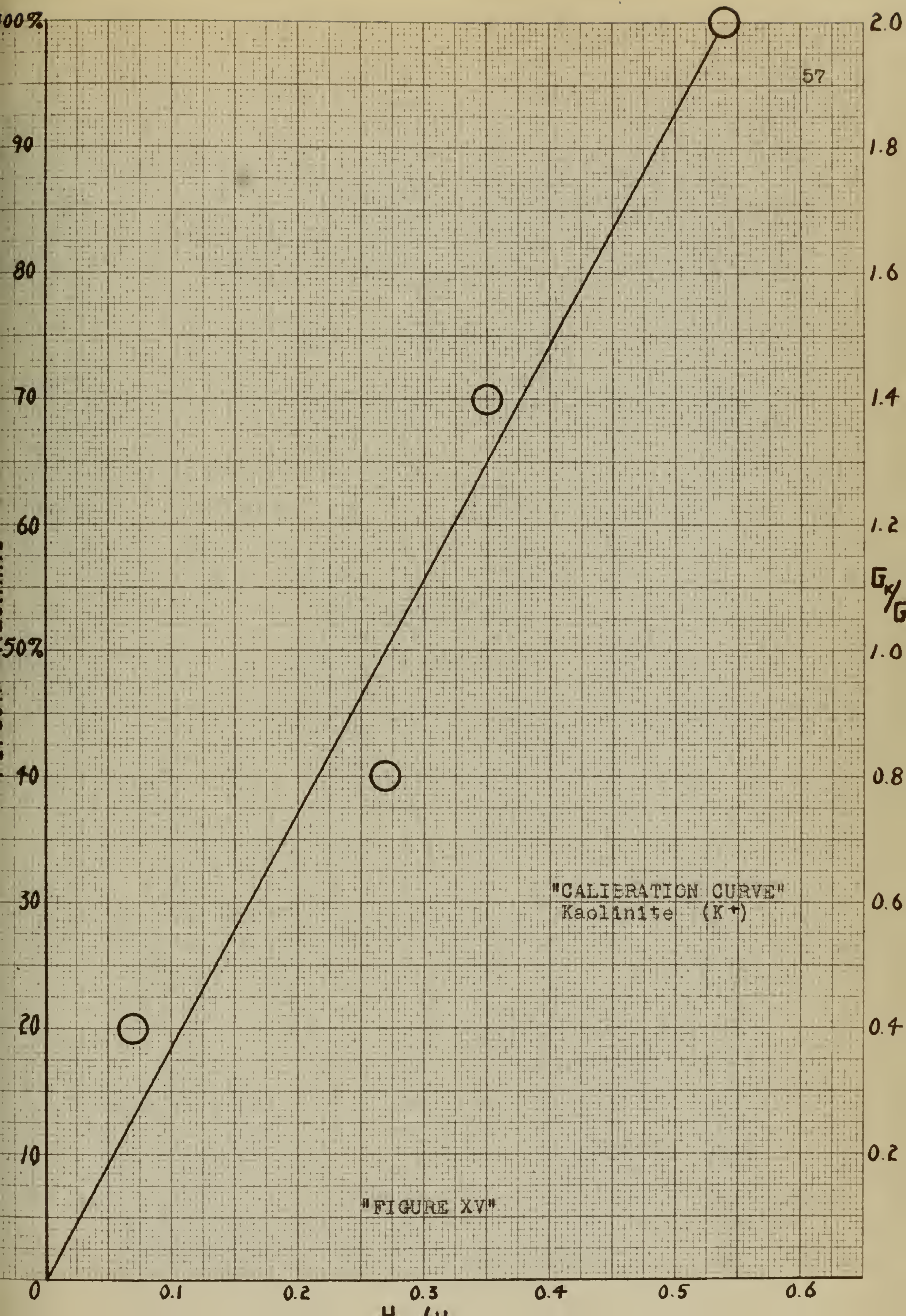
"FIGURE XIV"

Table 1

DATA ACCUMULATION

Kaolinite (K^{+}) and Internal-Standard

	G_K/G_s		Height of Peak			Ave.	H_K/H_s
K-I	2.00	Kaolinite	6.3	6.2	6.2	6.2	0.54
		Int. Std.	11.6	11.9	11.7	11.7	
K-II	1.40	Kaolinite	3.7	3.9	3.9	3.9	0.35
		Int. Std.	11.8	11.1	11.1	11.3	
K-III	0.80	Kaolinite	3.4	3.5	3.5	3.5	0.27
		Int. Std.	12.9	12.9	12.6	12.9	
K-IV	0.40	Kaolinite	0.8	0.6	0.7	0.7	0.07
		Int. Std.	9.6	10.1	9.8	9.8	



100%
90
80
70
60
50%
40
30
20
10
0
0.1
0.2
0.3
0.4
0.5
0.6
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Gx/G
"CALIBRATION CURVE"
Kaolinite (K+)

"FIGURE XV"

APPENDIX A

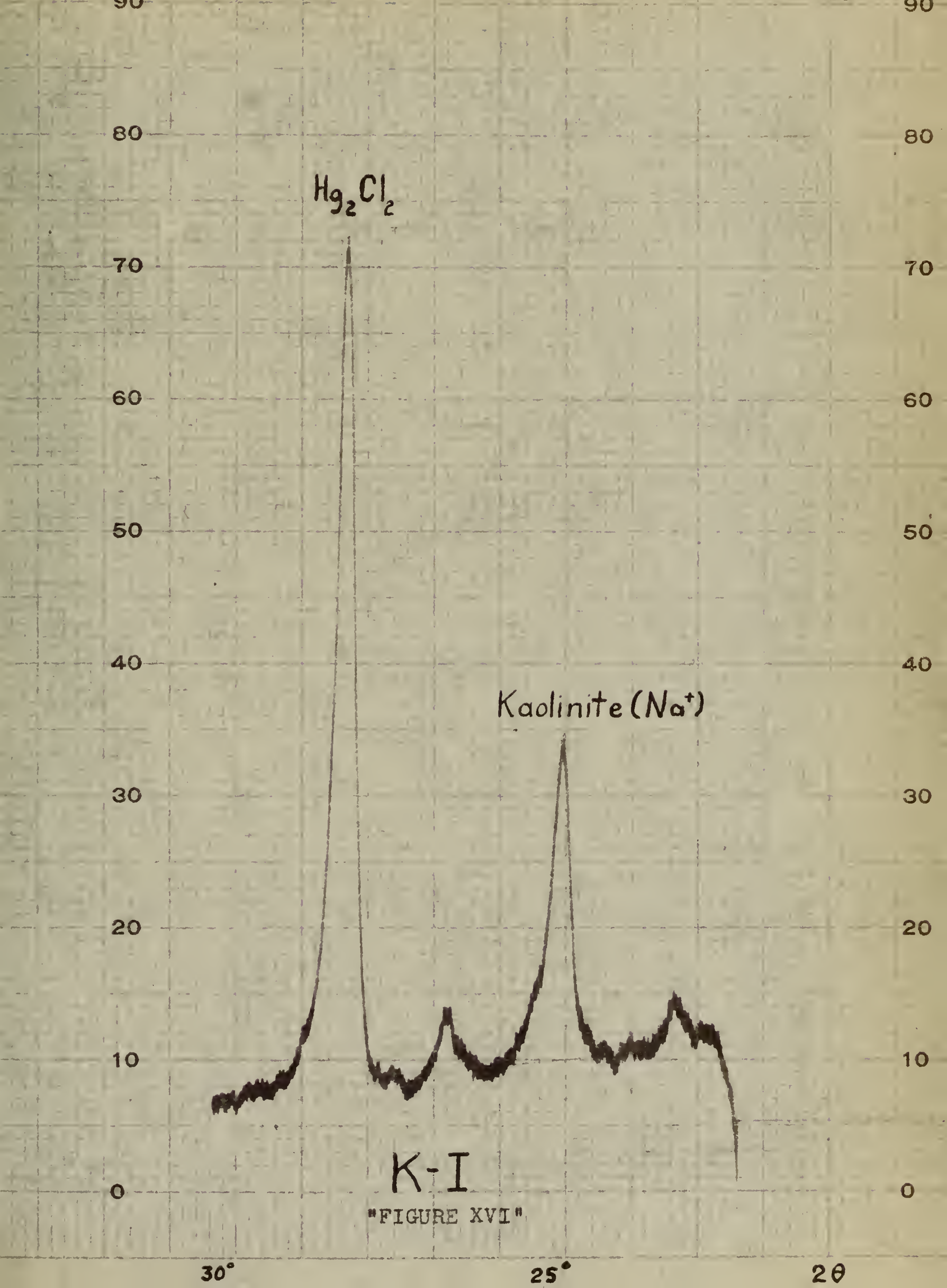
SECTION II

Ionic Saturation (Na^+)

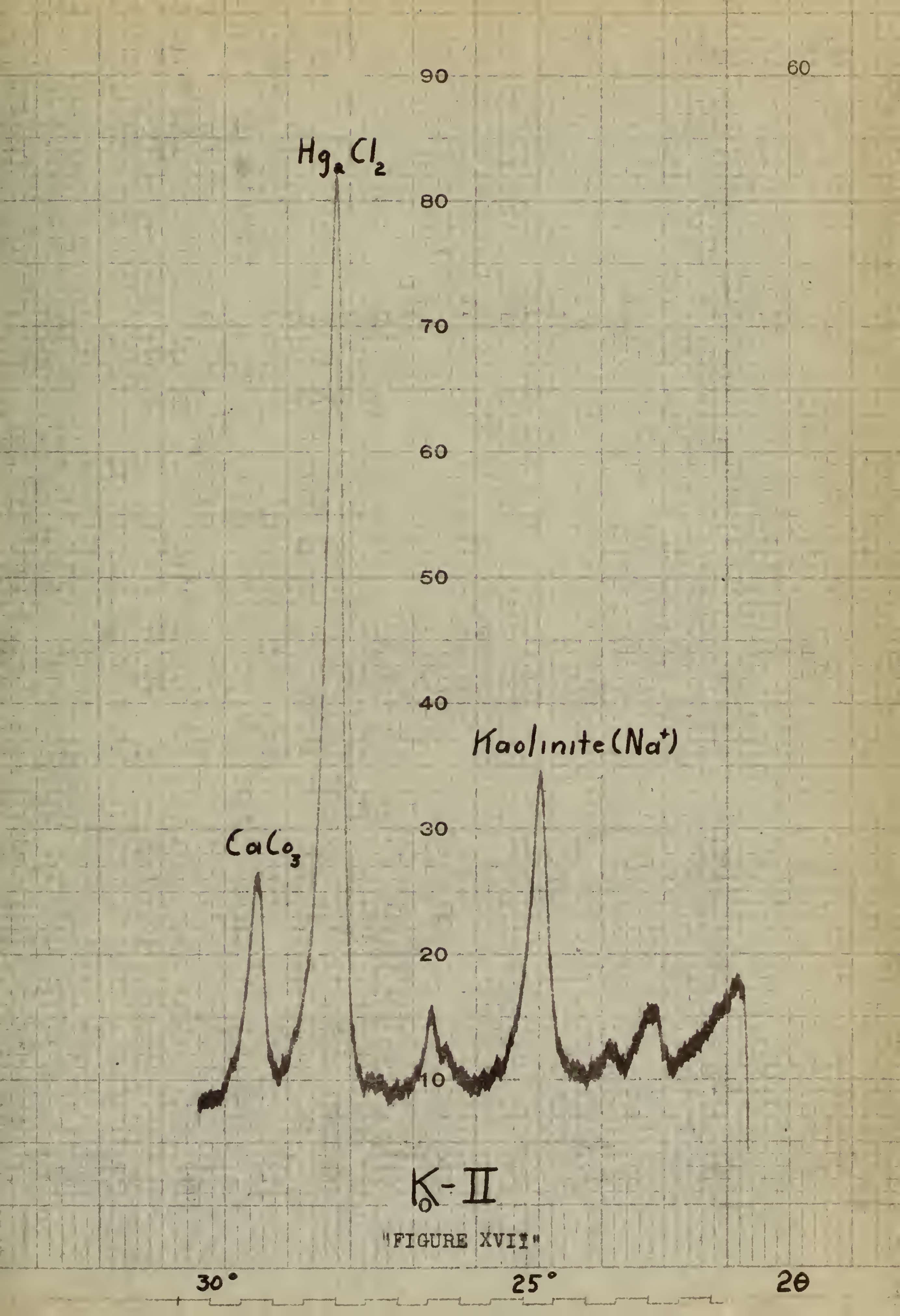
Mixtures:		Weight (grams) K-I	K-II	K-III
Clay Mineral	- Kaolinite (Na^+)	2.00	1.60	1.20
Diluent	- $CaCo_3$	0.00	0.40	0.80
Standard	- Hg_2Cl_2	1.00	1.00	1.00

Spectrometer Data

Same as Section I

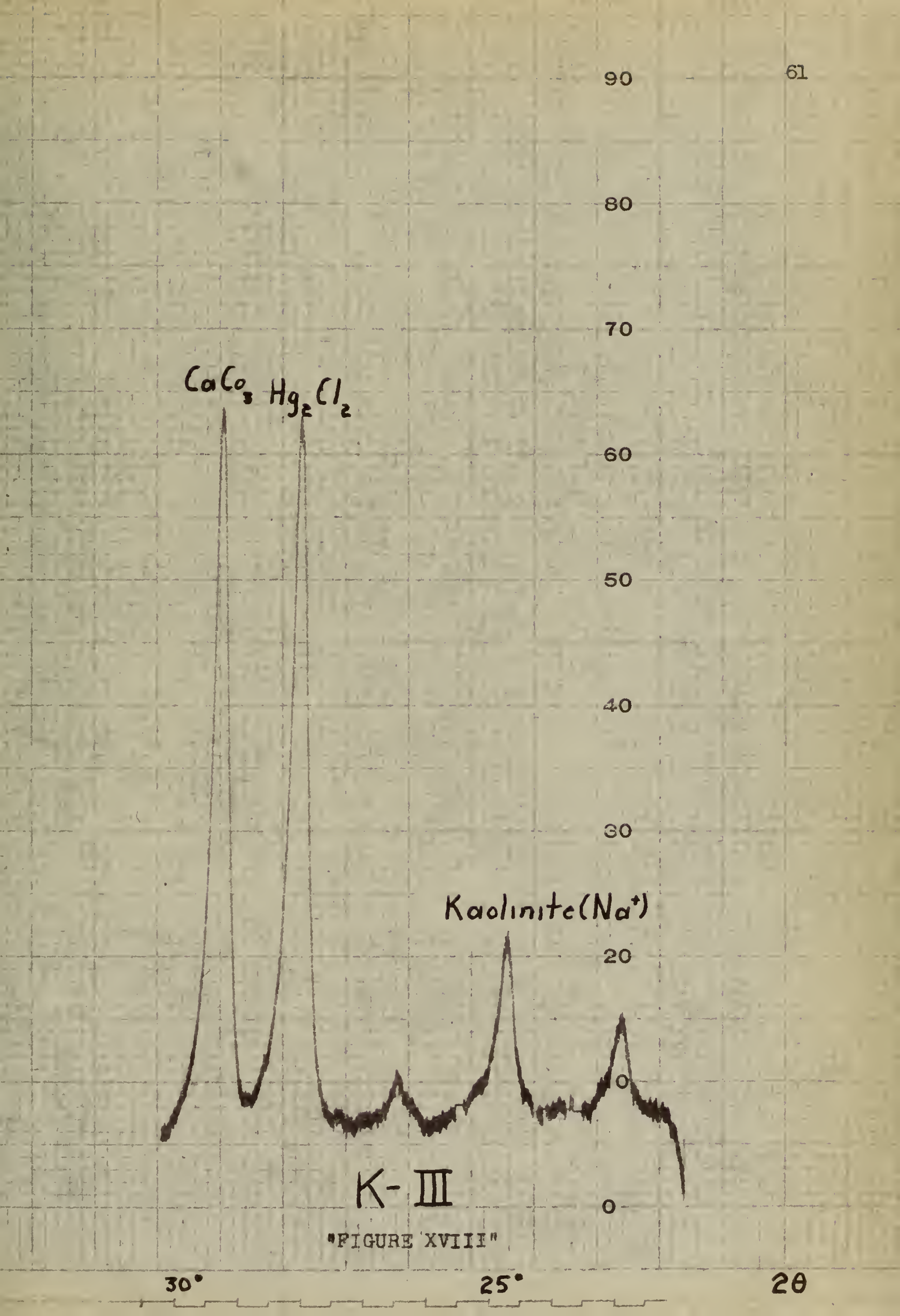


"FIGURE XVI"



K_0-II

"FIGURE XVII"



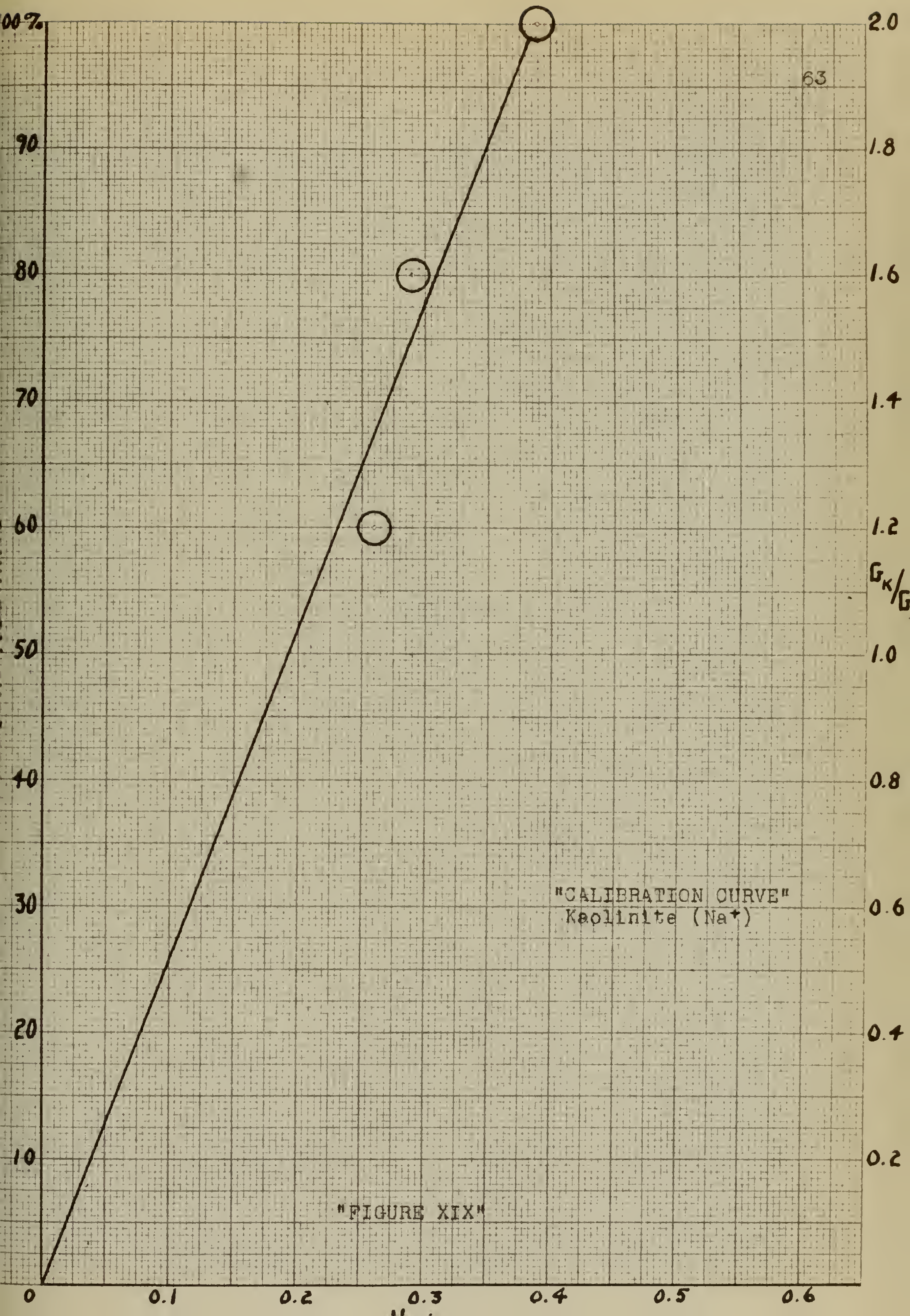
"FIGURE XVIII"

Table 2

DATA ACCUMULATION

Kaolinite (Na^+) and Internal-Standard

	G_K/G_S		Height of Peak			Average	H_K/H_S
K-I	2.00	Kaolinite	5.0	4.8	5.2	5.0	0.39
		Int. Std.	12.8	12.6	13.0	12.8	
K-II	1.00	Kaolinite	5.0	5.0	5.2	3.1	0.29
		Int. Std.	14.6	14.8	15.1	11.5	
K-III	1.20	Kaolinite	3.0	2.9	3.0	3.0	0.26
		Int. Std.	11.3	11.0	11.7	11.3	


100%
90
80
70
60
50
40
30
20
10
0
0.1
0.2
0.3
0.4
0.5
0.6
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
G_K/G
"CALIBRATION CURVE"
Kaolinite (Na^+)

"FIGURE XIX"

APPENDIX A

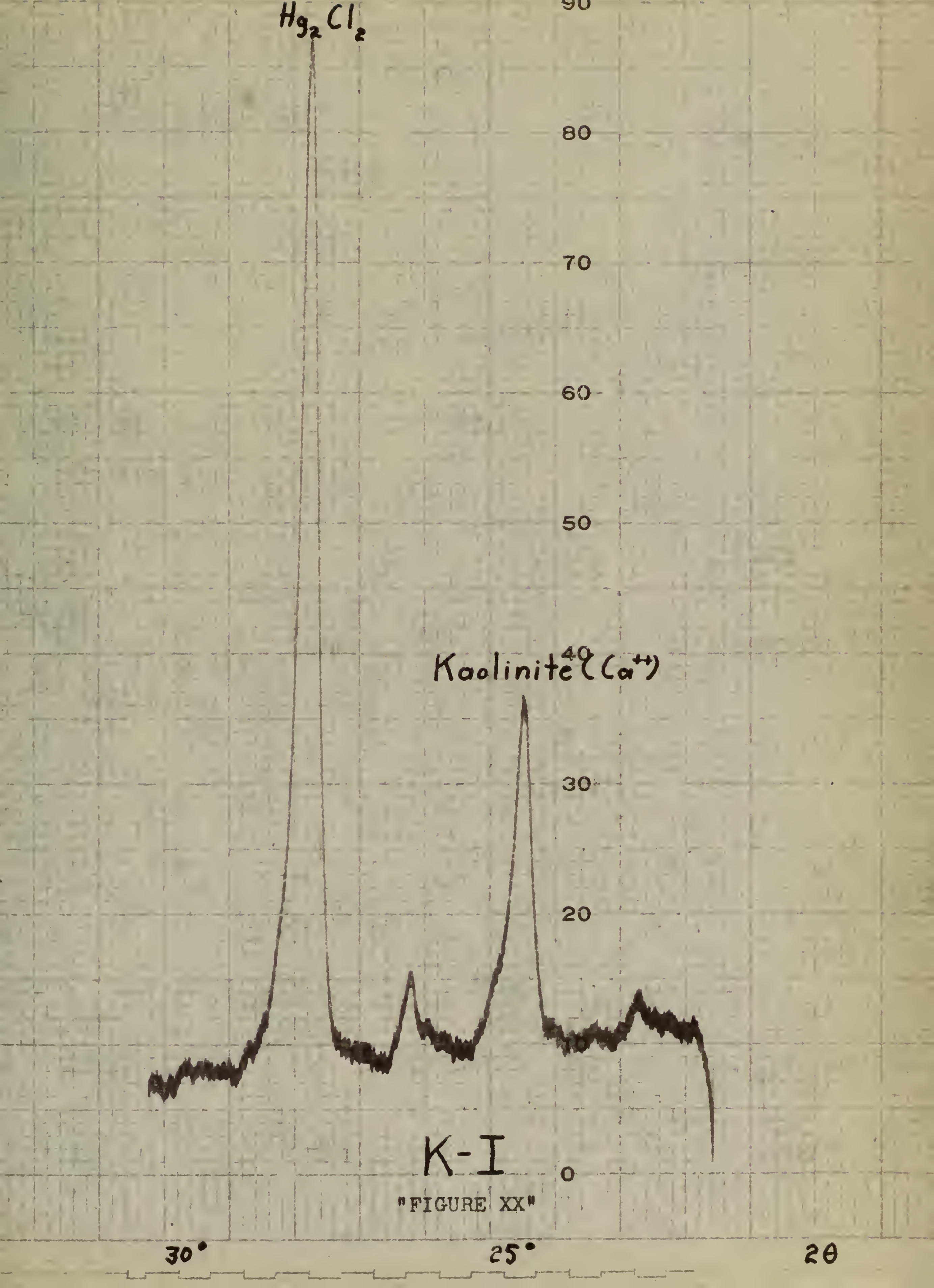
SECTION III

Ionic Saturation (Ca^{++})

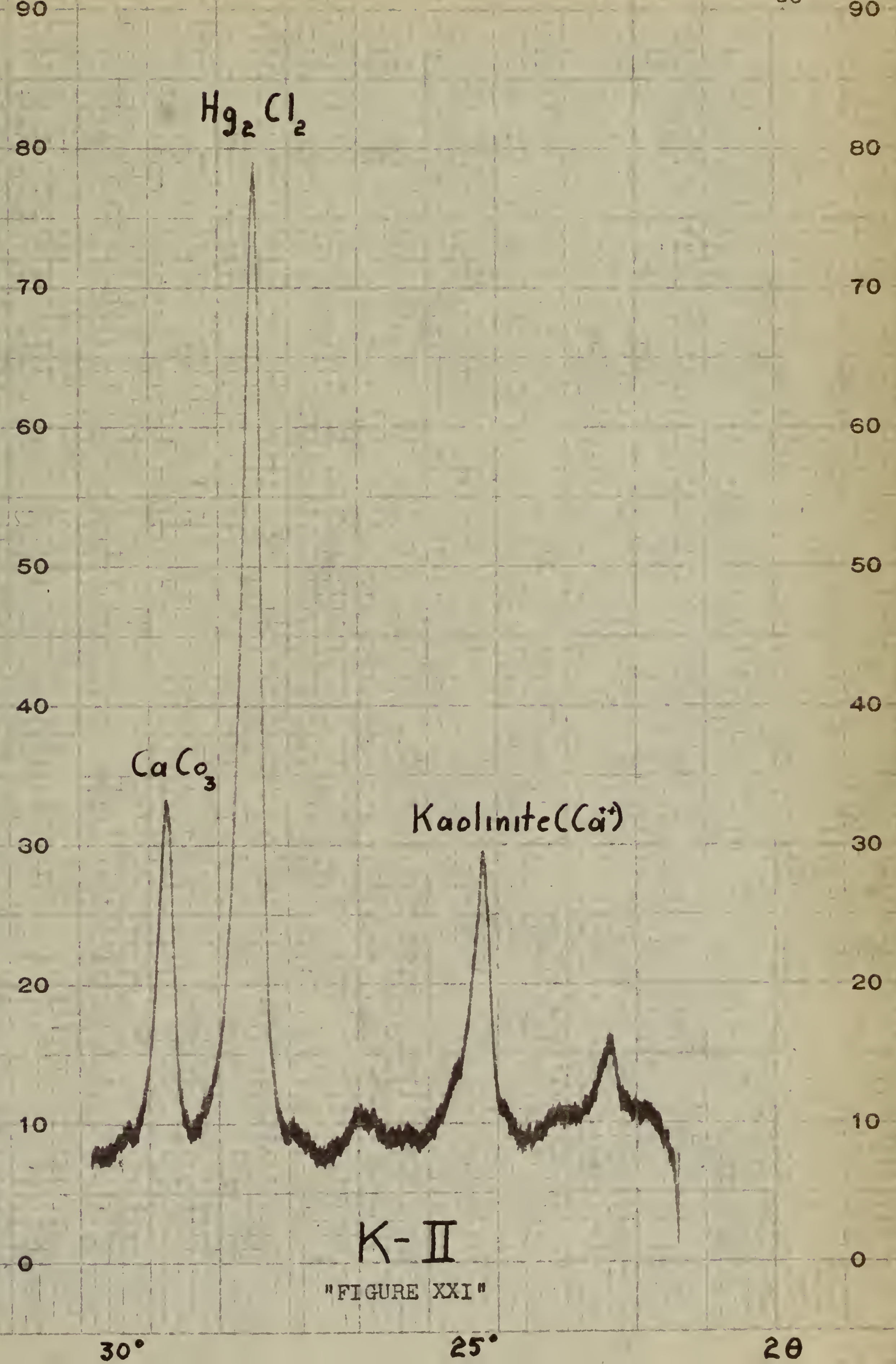
Mixtures:		Weight (grams)			
		K-I	K-II	K-III	K-IV
Clay Mineral	- Kaolinite (Ca^{++})	2.00	1.40	0.80	0.40
Diluent	- $CaCo_3$	0.00	0.60	1.20	1.60
Standard	- Hg_2Cl_2	1.00	1.00	1.00	1.00

Spectrometer Data

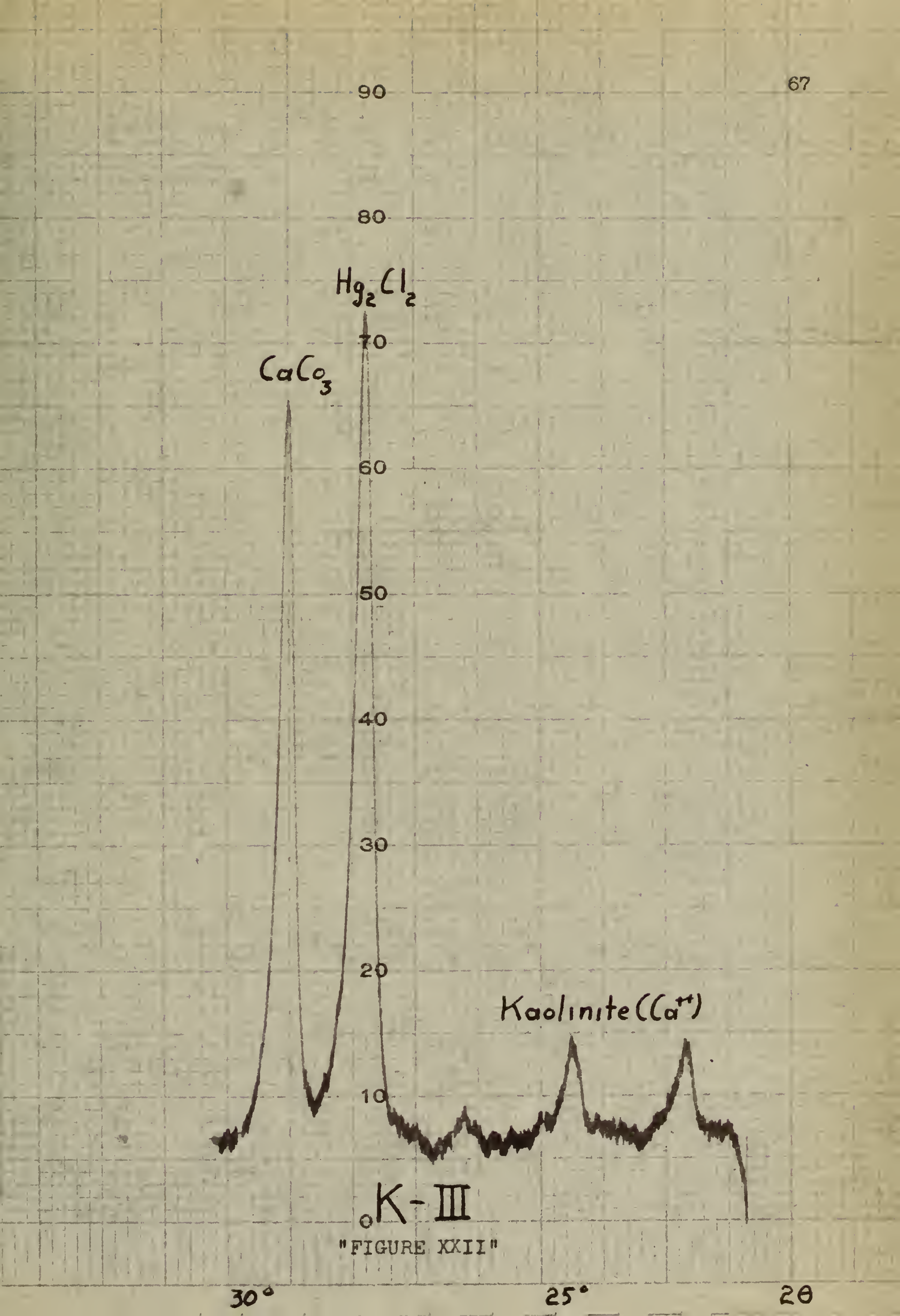
Same as Section I



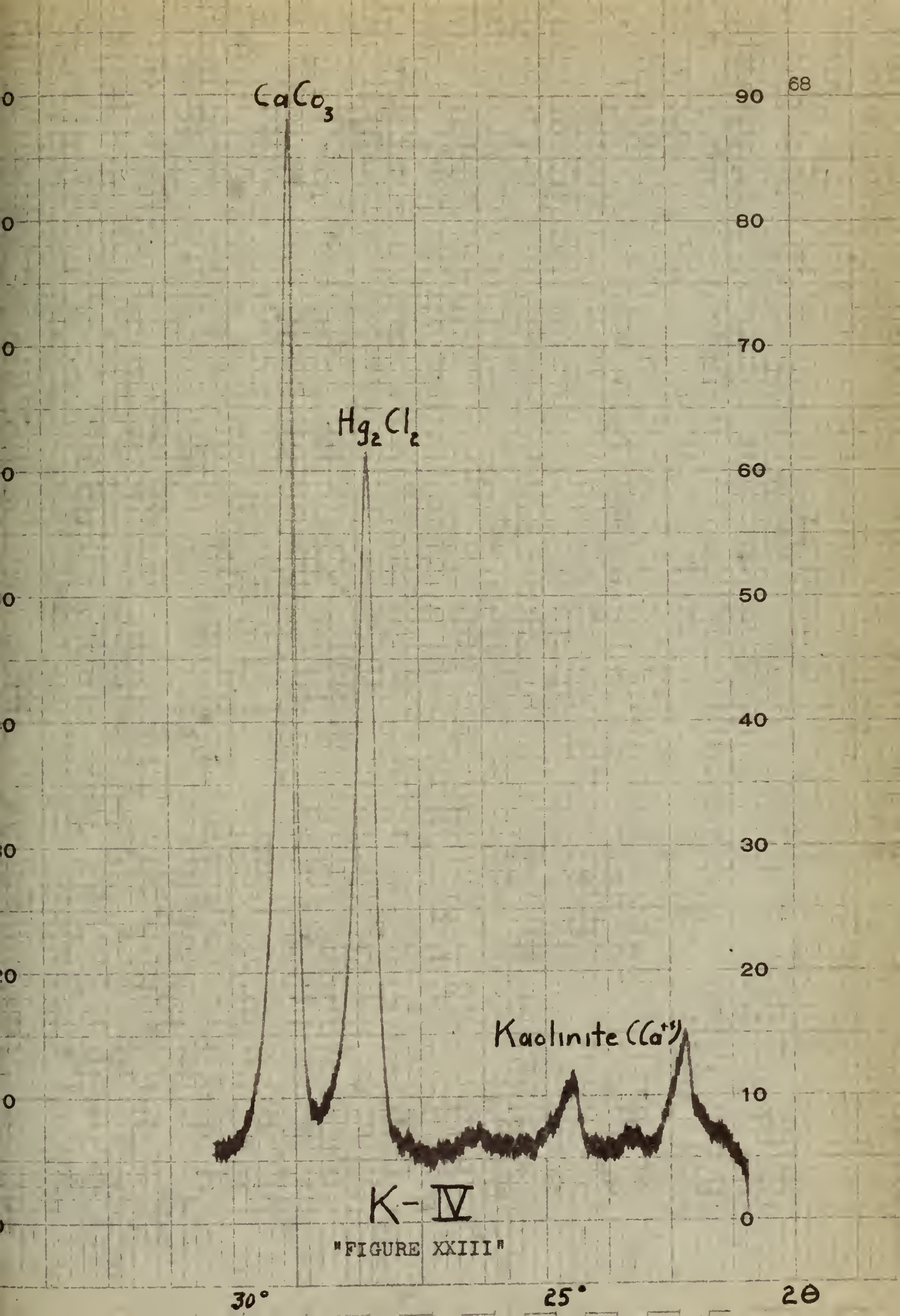
"FIGURE XX"


90
80
70
60
50
40
30
20
10
0
Hg_2Cl_2
$CaCO_3$
Kaolinite (Ca^{++})
K-II
30°
25°
2θ

"FIGURE XXI"


90
80
Hg_2Cl_2
70
$CaCO_3$
60
50
40
30
20
10
0
Kaolinite (Ca^{++})
K-III
30°
25°
2θ

"FIGURE XXII"



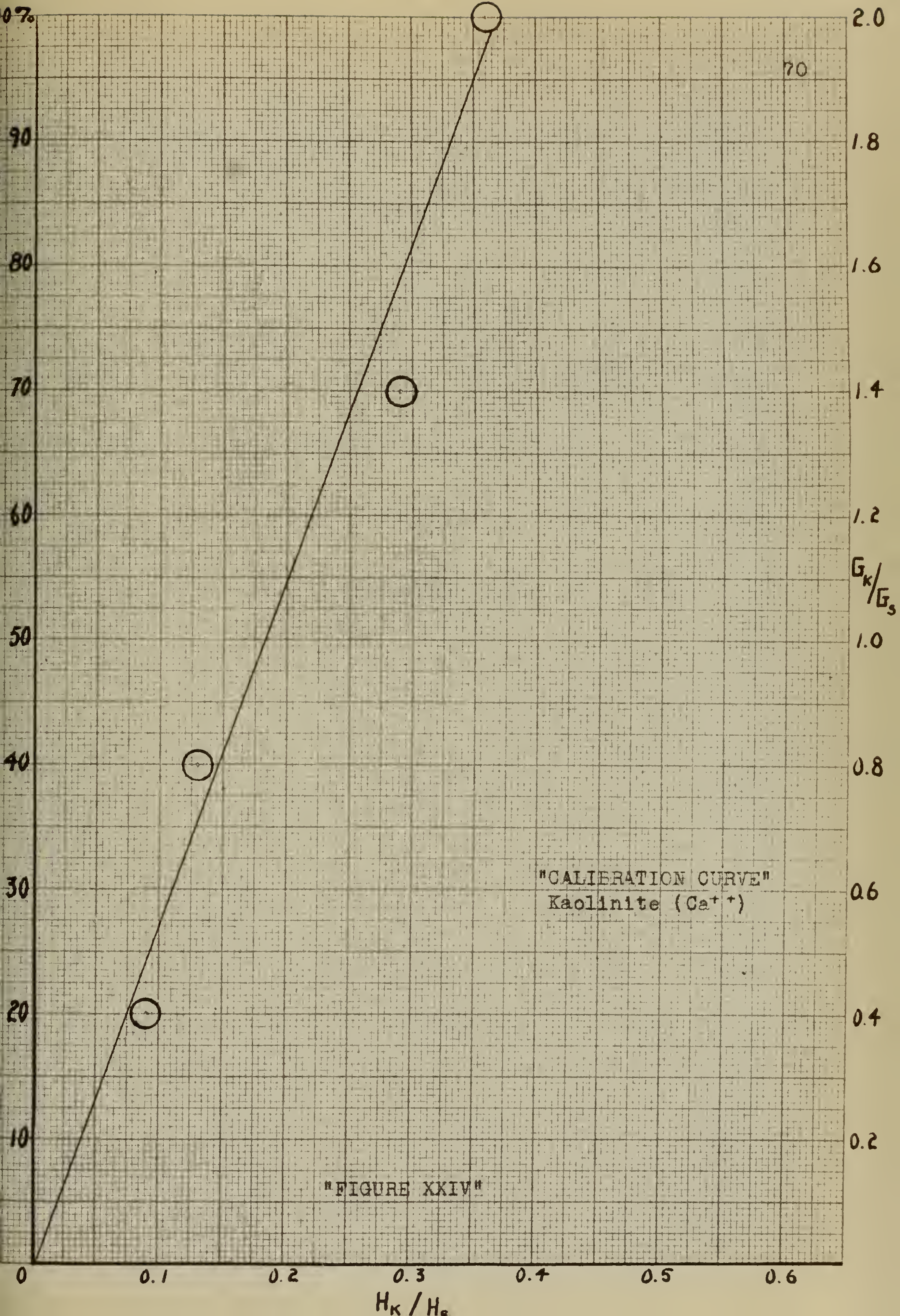
"FIGURE XXIII"

Table 3

<u>DATA ACCUMULATION</u>

Kaolinite (Ca^{++}) and Internal-Standard

	G_K/G_S		Height of Peak			Ave.	H_K/H_S
K-I	2.00	Kaolinite	5.3	5.6	5.7	5.5	0.36
		Int. Std.	15.5	15.2	15.4	15.3	
K-II	1.40	Kaolinite	4.1	4.0	4.0	4.0	0.29
		Int. Std.	14.0	13.[illegible]	13.7	13.6	
K-III	0.80	Kaolinite	1.7	1.7	1.8	1.7	0.13
		Int. Std.	13.3	1[illegible].9	13.3	13.3	
K-IV	0.40	Kaolinite	1.1	1.2	1.0	1.1	0.09
		Int. Std.	11.2	11.2	11.1	11.2	



70
%
90
80
70
60
50
40
30
20
10
0
0.1
0.2
0.3
0.4
0.5
0.6
H_K / H_s
2.0
1.8
1.6
1.4
1.2
G_K/G_s
1.0
0.8
0.6
0.4
0.2
"CALIBRATION CURVE"
Kaolinite (Ca^{++})
"FIGURE XXIV"

APPENDIX A

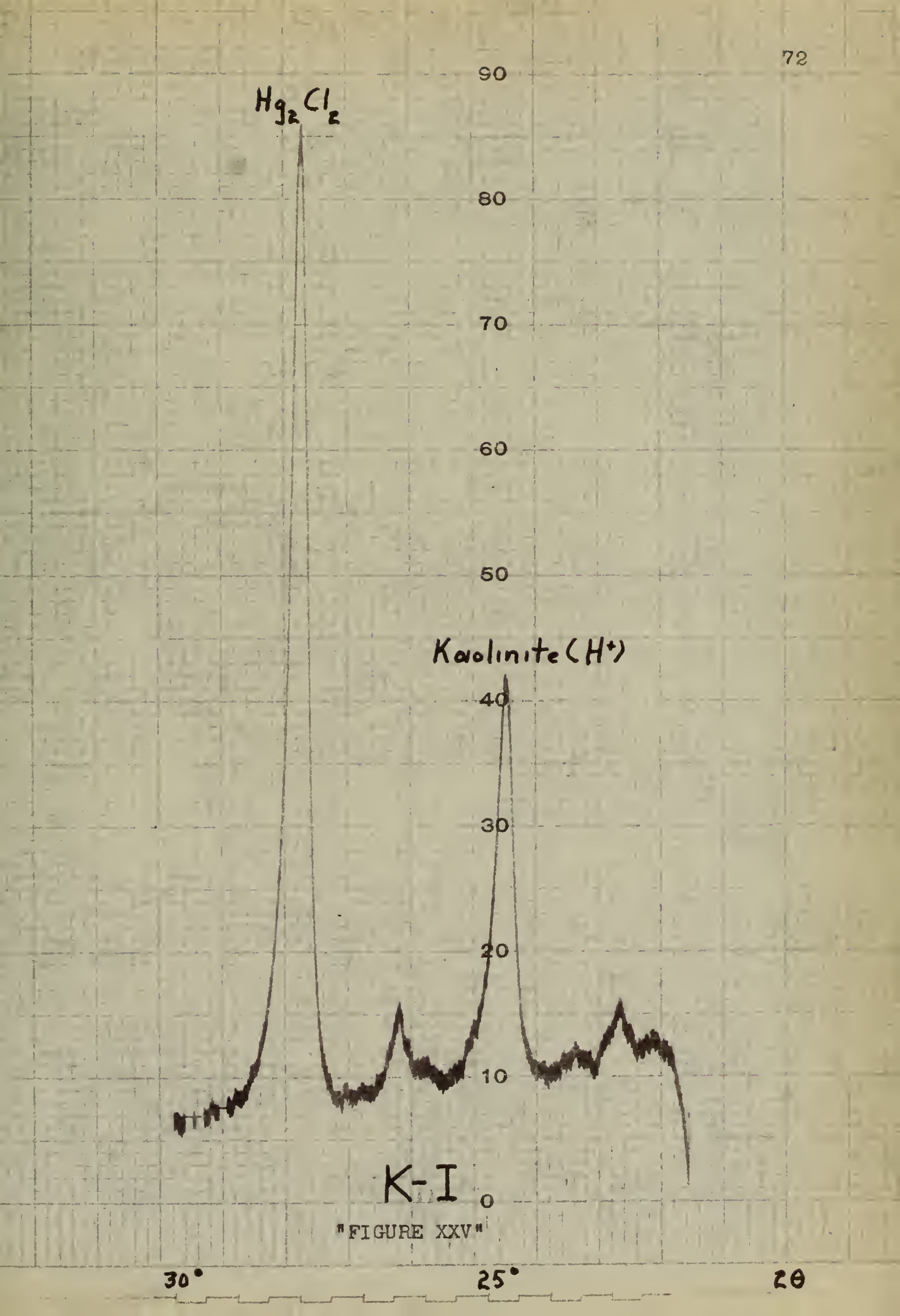
SECTION IV

Ionic Saturation (H^+)

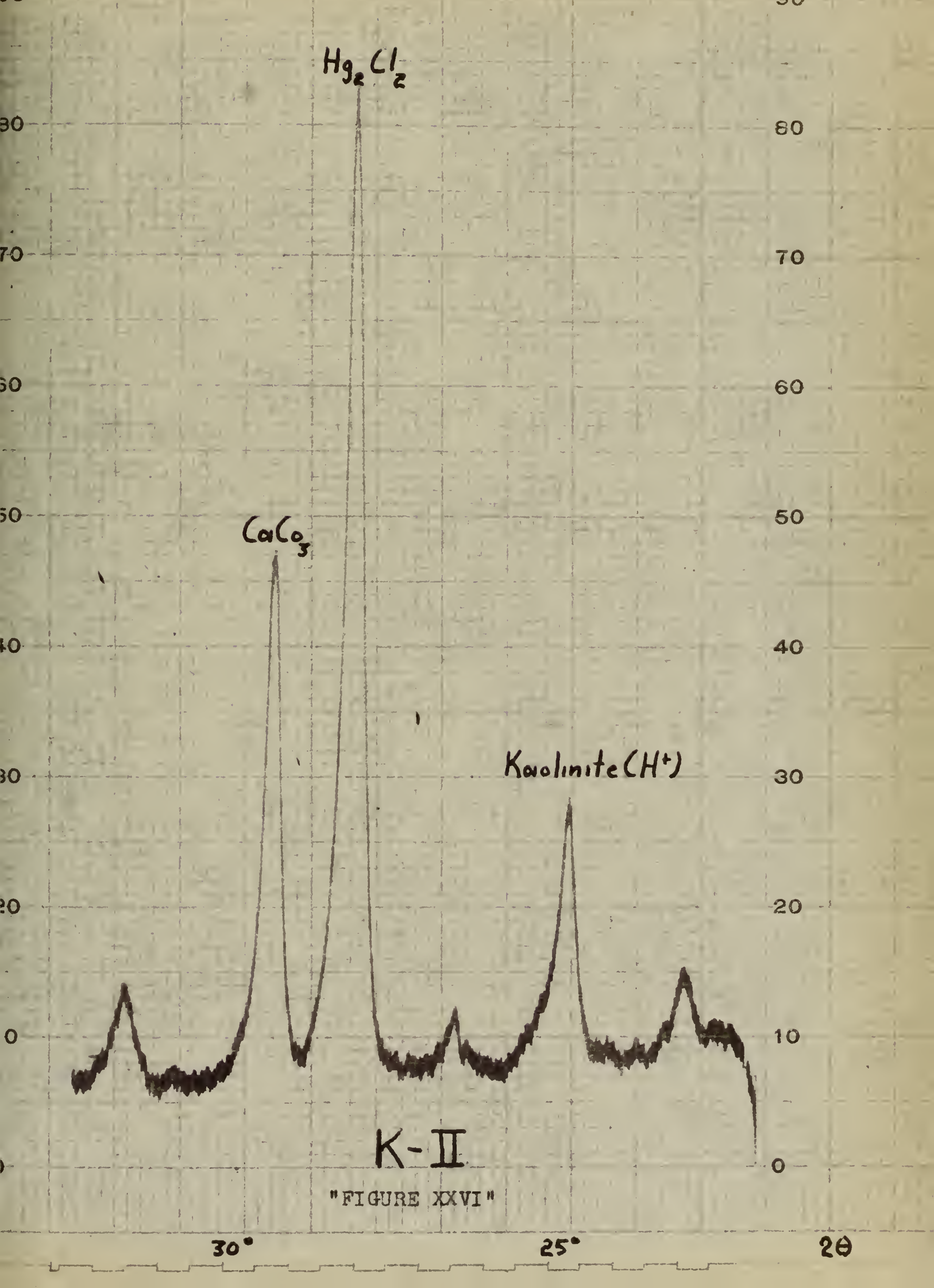
Mixtures:		Weight (grams)			
		K-I	K-II	K-III	K-IV
Clay Mineral	- Kaolinite (H^+)	2.00	1.40	0.80	0.40
Diluent	- $CaCo_3$	0.00	0.60	1.20	1.60
Standard	- Hg_2Cl_2	1.00	1.00	1.00	1.00

Spectrometer Data

Same as Section I

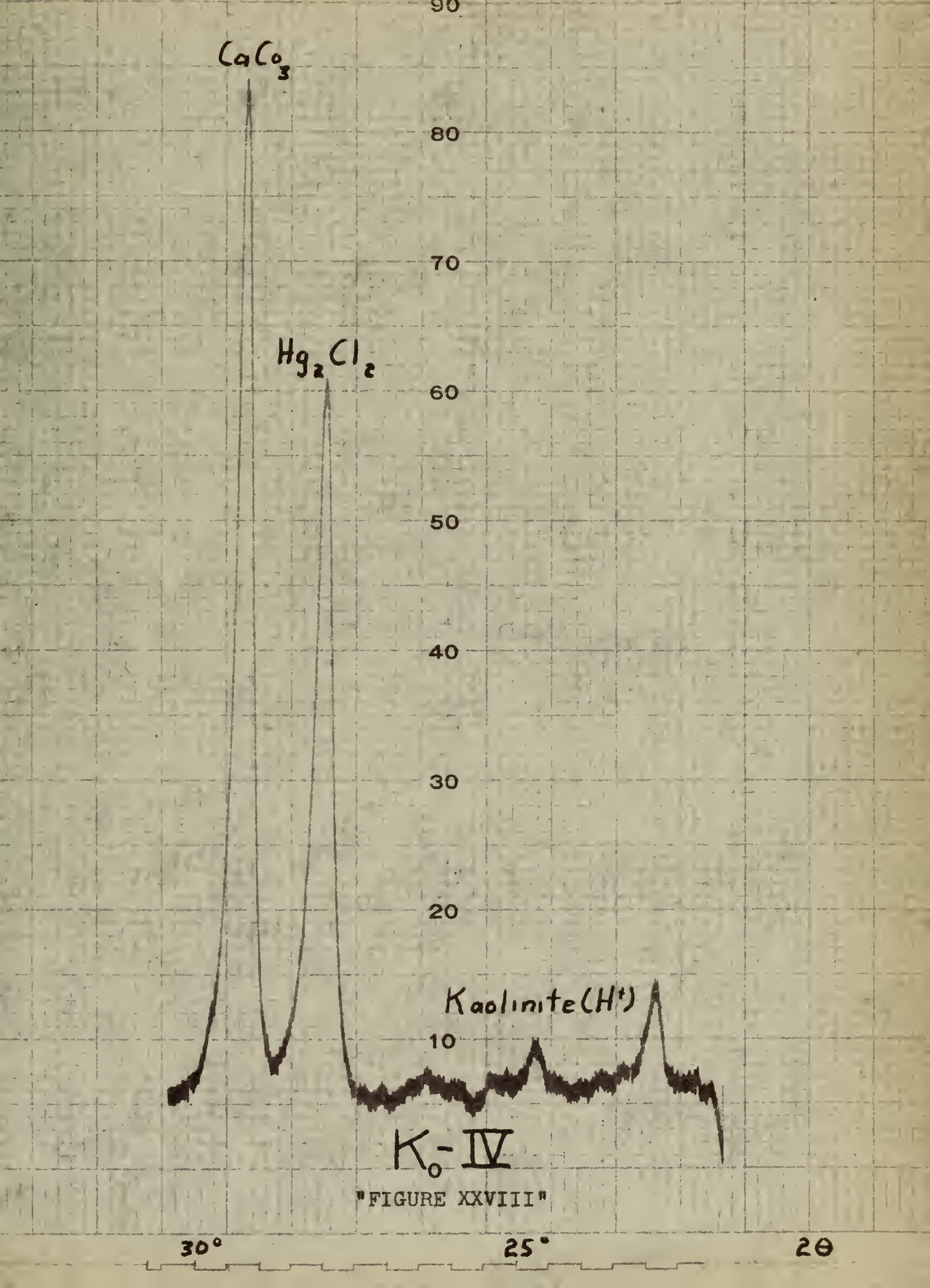


"FIGURE XXV"



"FIGURE XXVI"

"FIGURE XXVII"



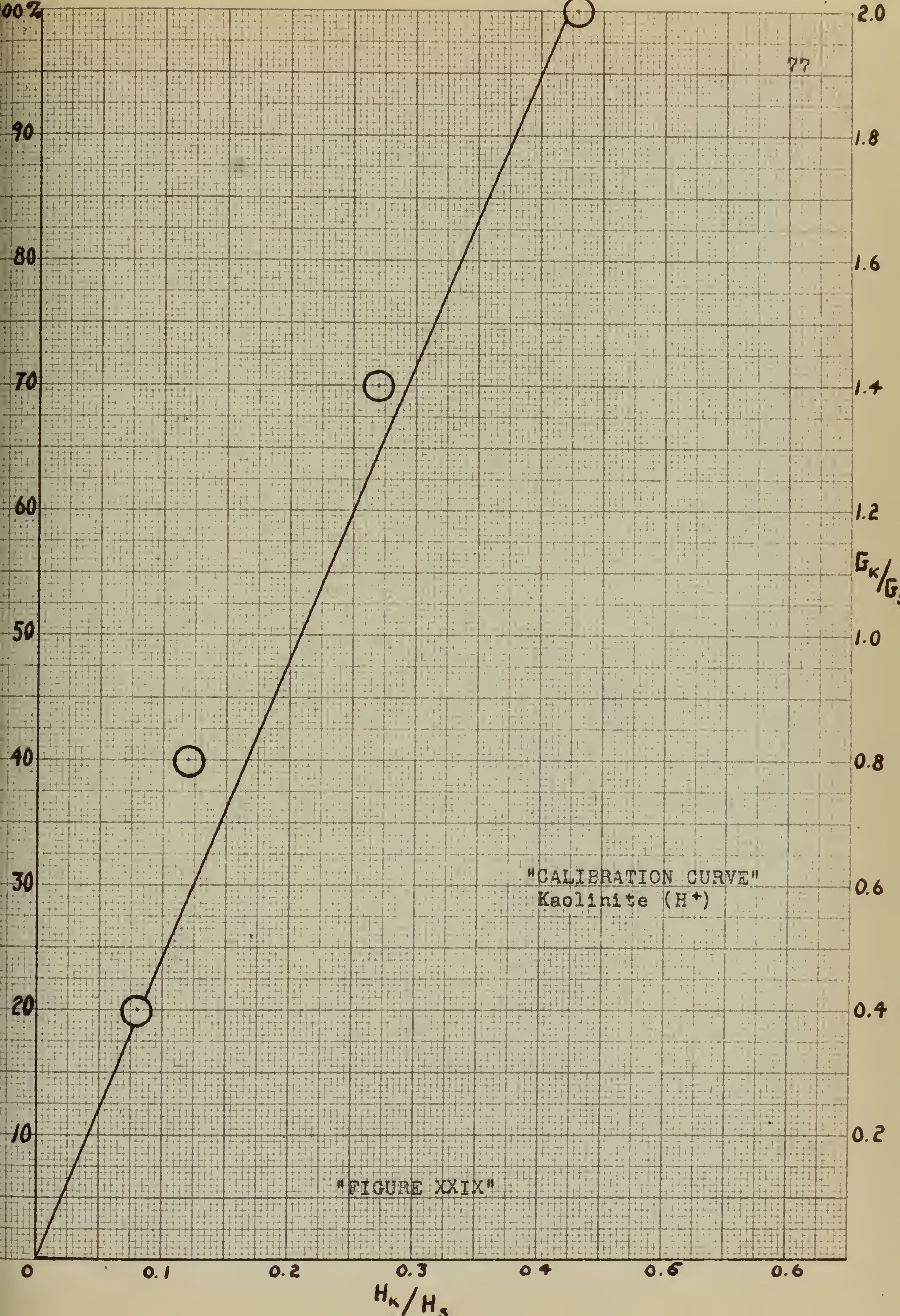
"FIGURE XXVIII"

Table 4

DATA ACCUMULATION

Kaolinite (H^+) and Internal-Standard

	G_K/G_S		Height of Peak			Ave.	H_K/H_S
K-I	2.00	Kaolinite	6.4	6.6	7.0	6.7	0.43
		Int. Std.	15.5	15.6	16.1	15.7	
K-II	1.40	Kaolinite	4.1	4.1	4.2	4.1	0.27
		Int. Std.	15.1	15.4	15.8	15.4	
K-III	0.80	Kaolinite	1.7	1.8	1.7	1.7	0.12
		Int. Std.	14.1	13.5	13.4	13.7	
K-IV	0.40	Kaolinite	0.8	1.0	1.0	0.9	0.08
		Int. Std.	11.0	11.2	11.3	11.2	


100%
90
80
70
60
50
40
30
20
10
0
0.1
0.2
0.3
0.4
0.5
0.6
H_K/H_S
2.0
1.8
1.6
1.4
1.2
G_K/G_S
1.0
0.8
0.6
0.4
0.2
"CALIBRATION CURVE"
Kaolinite (H^+)

"FIGURE XXIX"

APPENDIX B

Diffraction Strip Charts and Calibration Curves for Illite with Internal Standard

Clay Mineral	-	Morris, Illinois, Illite
Internal Standard	-	Mercurous Chloride
Diluent	-	Calcium Carbonate

APPENDIX B

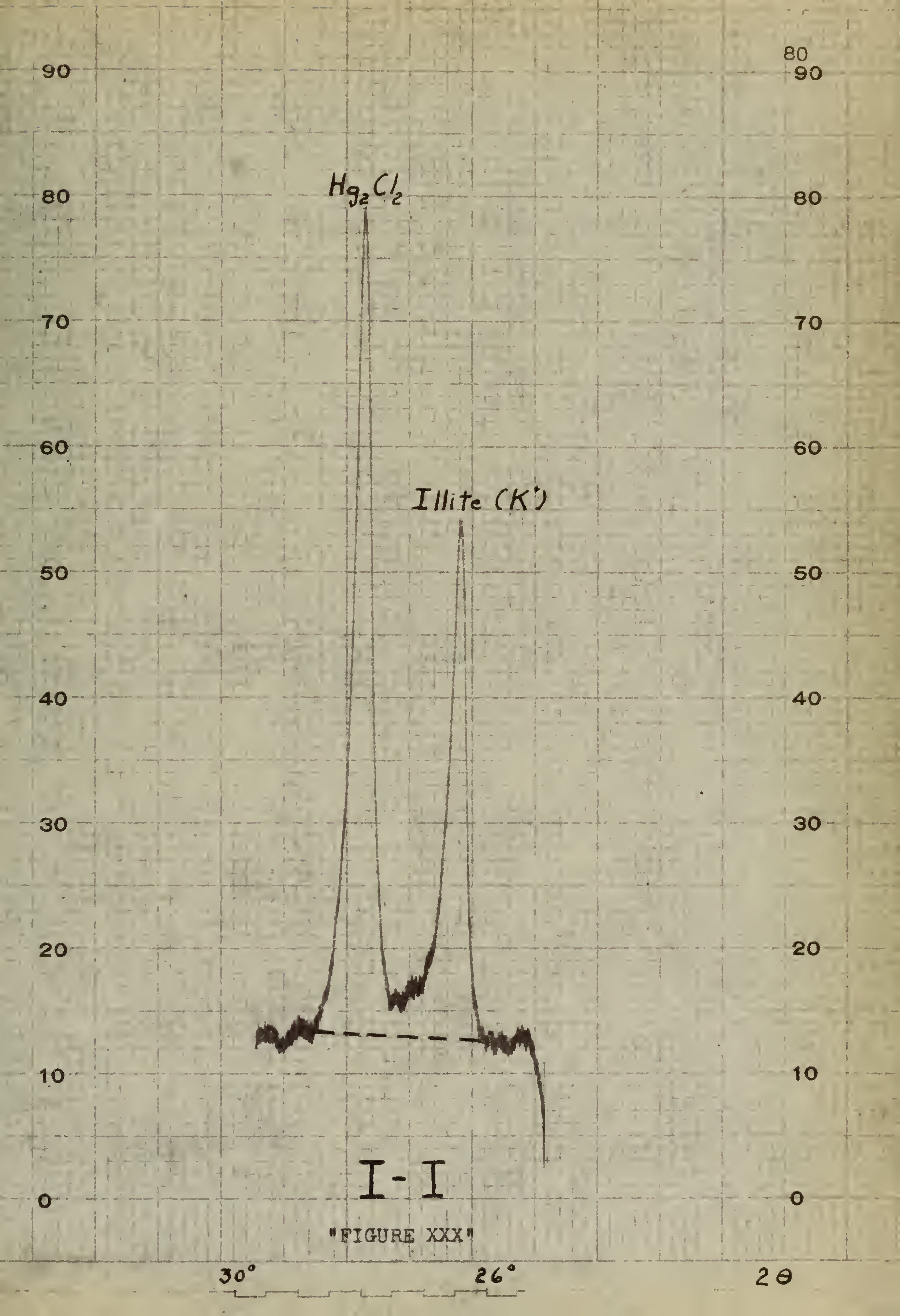
SECTION I

Ionic Saturation (K^+)

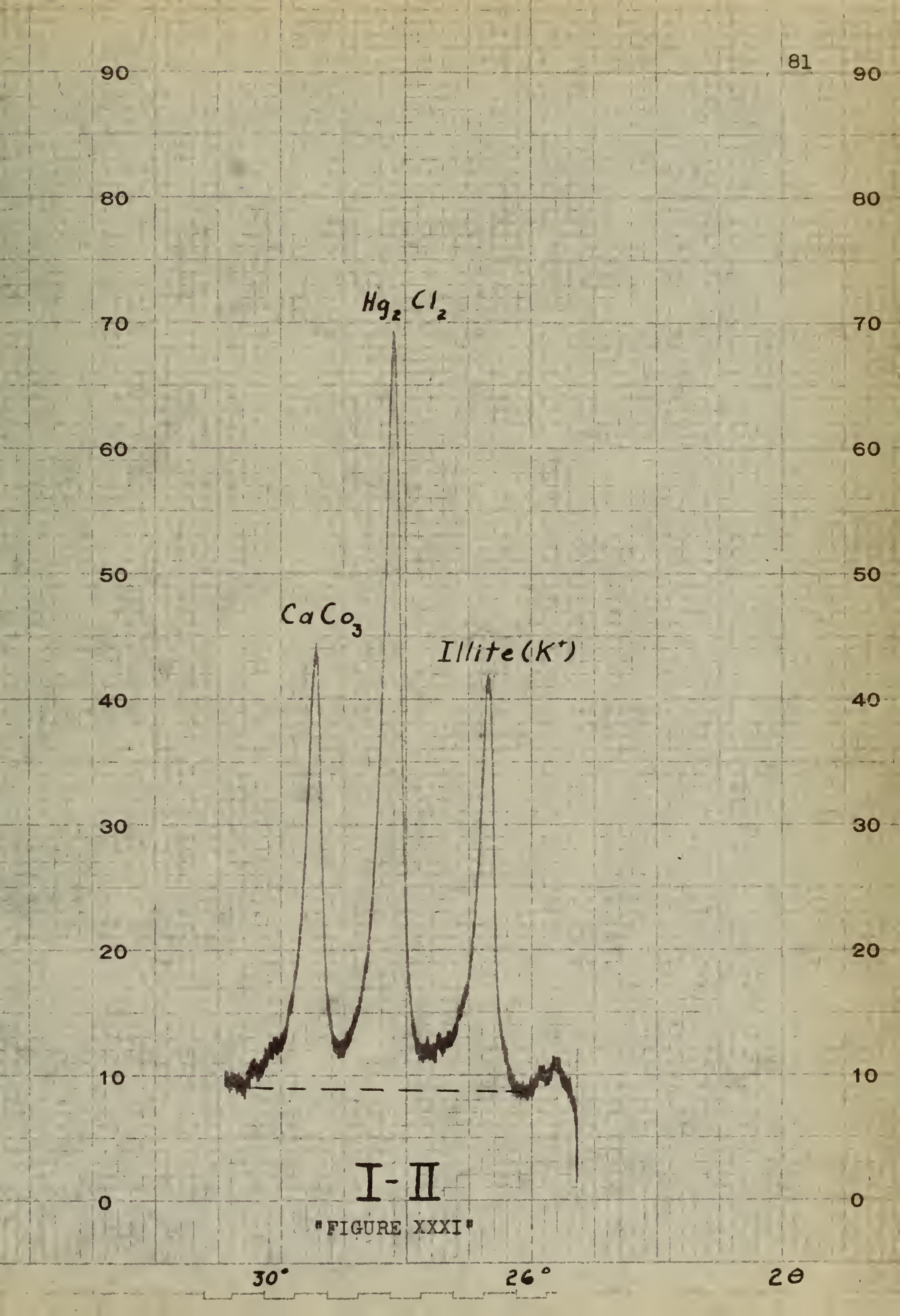
Mixtures:		Weight (grams)			
		I-I	I-II	I-III	I-IV
Clay Mineral	- Illite (K^+)	2.00	1.40	0.80	0.40
Diluent	- $CaCo_3$	0.00	0.60	1.20	1.60
Standard	- Hg_2Cl_2	1.00	1.00	1.00	1.00

Spectrometer Data

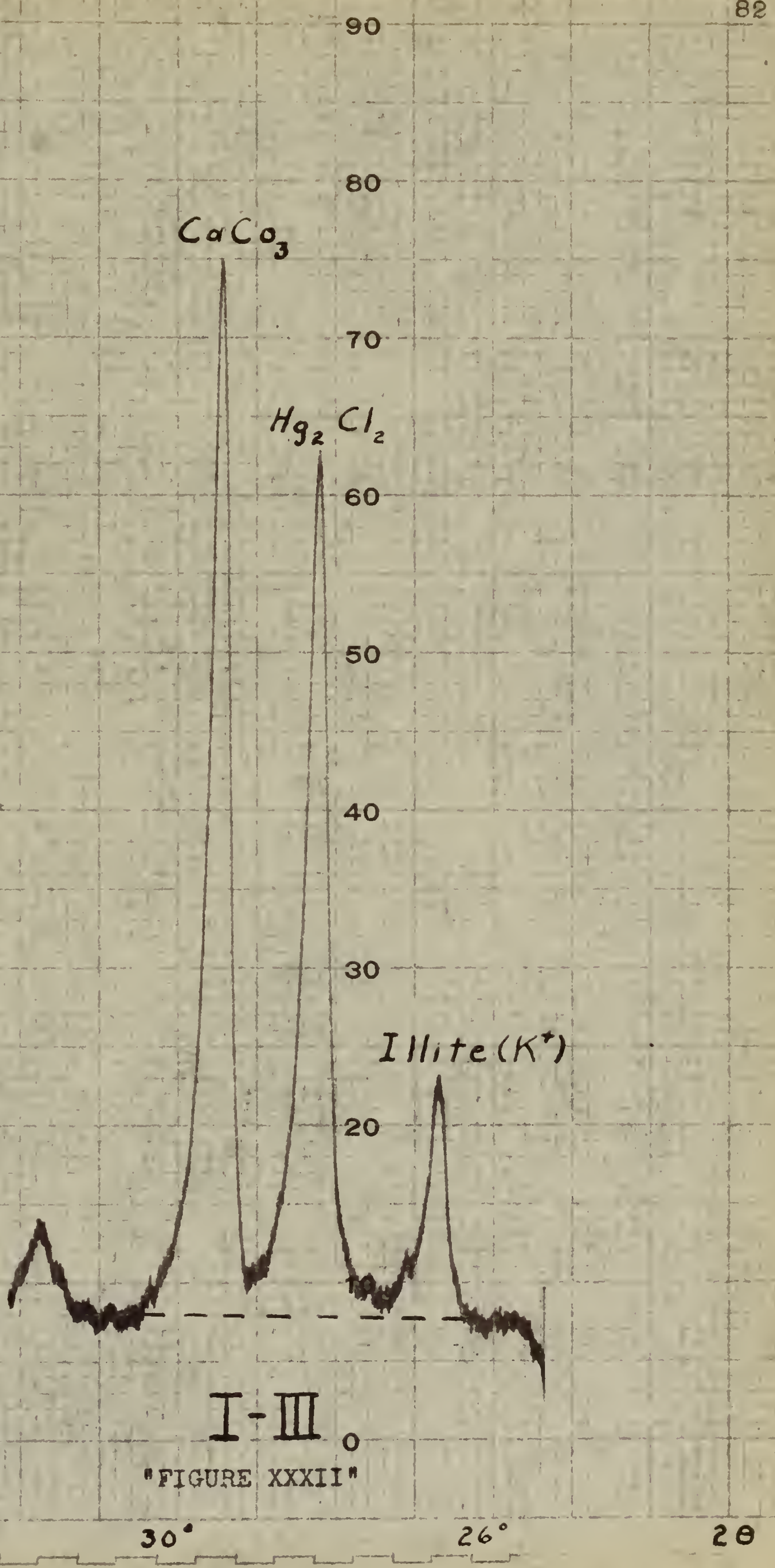
Radiation:	Copper
Filter:	Nickel
KVP:	70
Scanning Speed:	$1^\circ(2\theta)$/MIN.
Rate Meter:	SF 8
	M 0.6
	TC 8



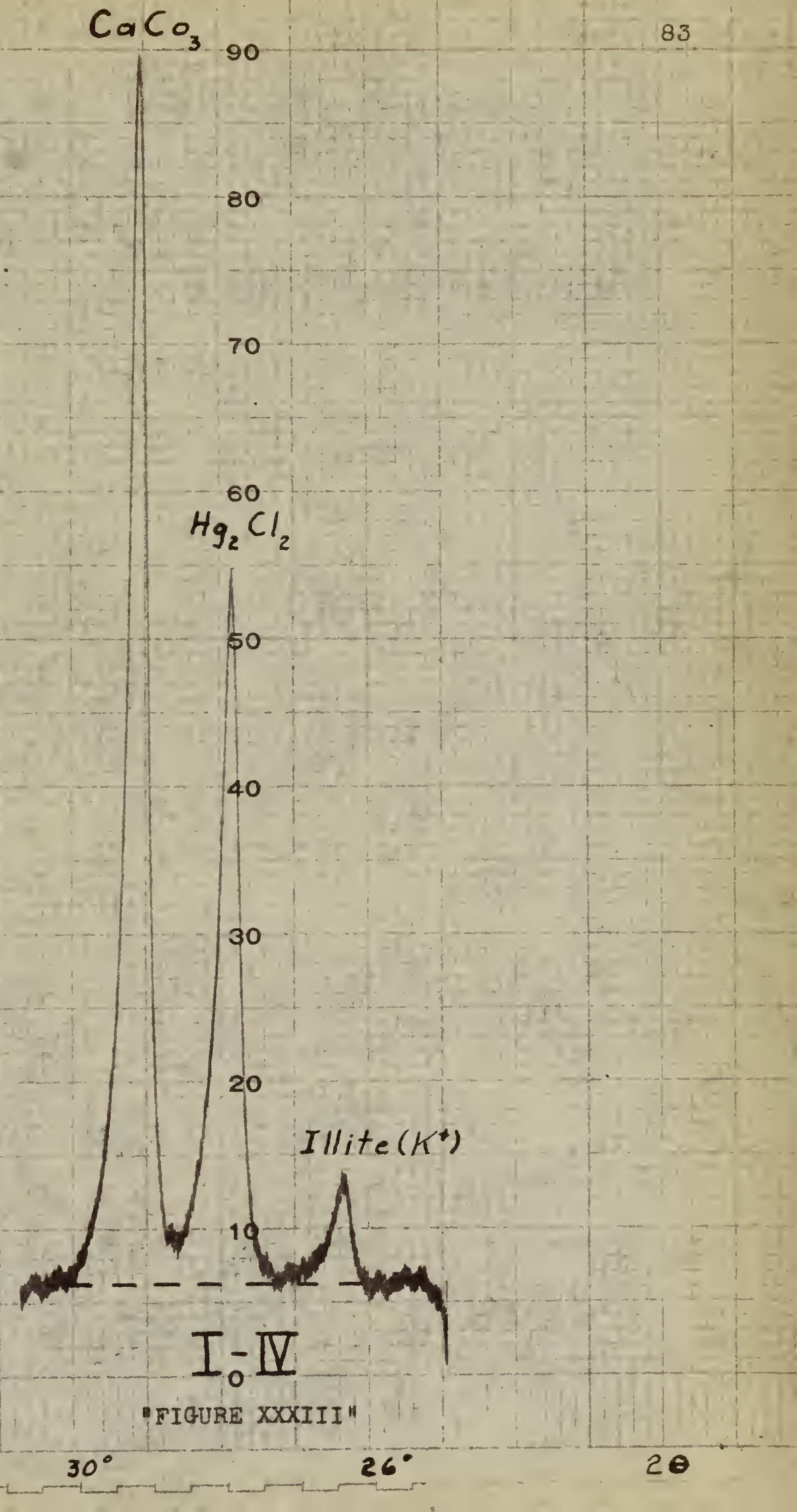
"FIGURE XXX"



"FIGURE XXXI"



"FIGURE XXXII"



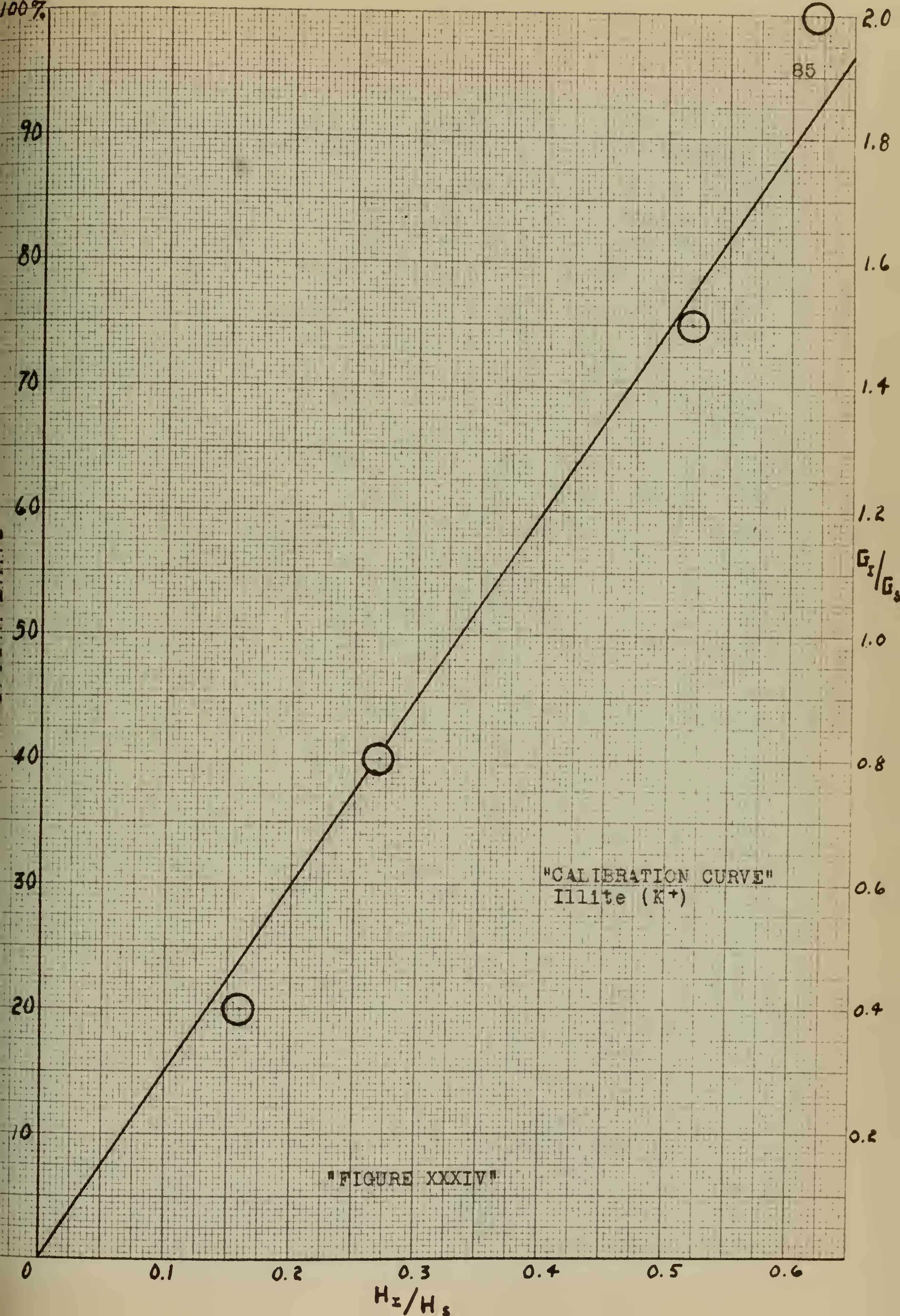
"FIGURE XXXIII"

Table 5

DATA ACCUMULATION

Illite (K^+) and Internal-Standard

	G_I/G_s	Mixture	Height of Peak			Ave.	H_I/H_s
I · I	2.00	Illite	9.3	[illegible].0	8.6	8.3	0.62
		Ca Co_3	13.2	13.3	13.4	13.3	
I · II	1.40	Illite	6.6	6.1	6.3	6.3	0.52
		Ca Co_3	12.1	12.0	11.6	11.9	
I · III	0.80	Illite	3.1	3.0	3.0	3.0	0.27
		Ca Co_3	11.0	10.6	11.1	10.9	
I · IV	0.40	Illite	1.5	1.5	1.5	1.5	0.16
		Ca Co_3	9.0	9.7	9.2	9.3	



100%
90
80
70
60
50
40
30
20
10
0
0.1
0.2
0.3
0.4
0.5
0.6
H_x/H_s
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
G_x/G_s
85
"CALIBRATION CURVE"
Illite (K^+)
"FIGURE XXXIV"

APPENDIX B

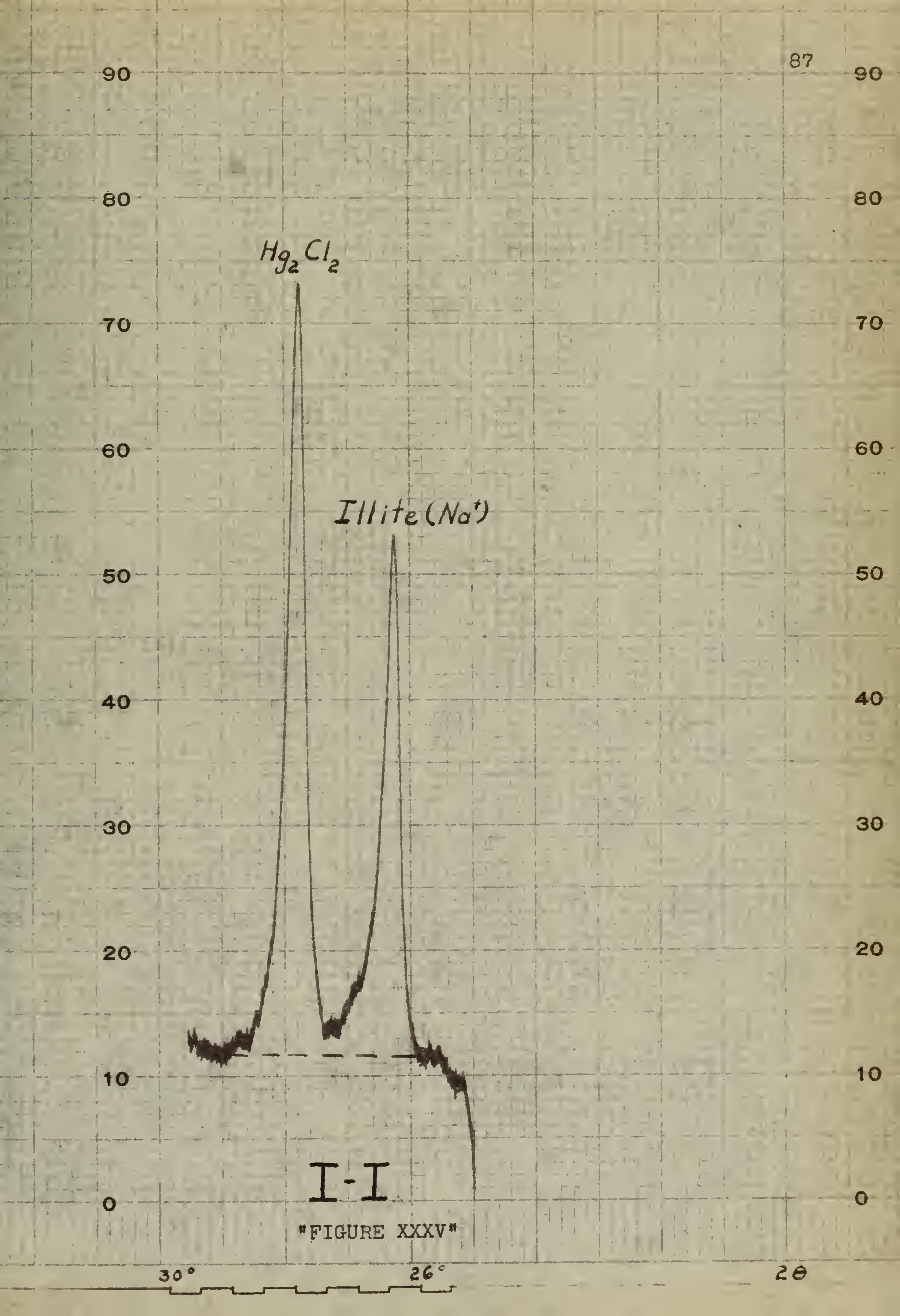
SECTION II

Ionic Saturation (Na^+)

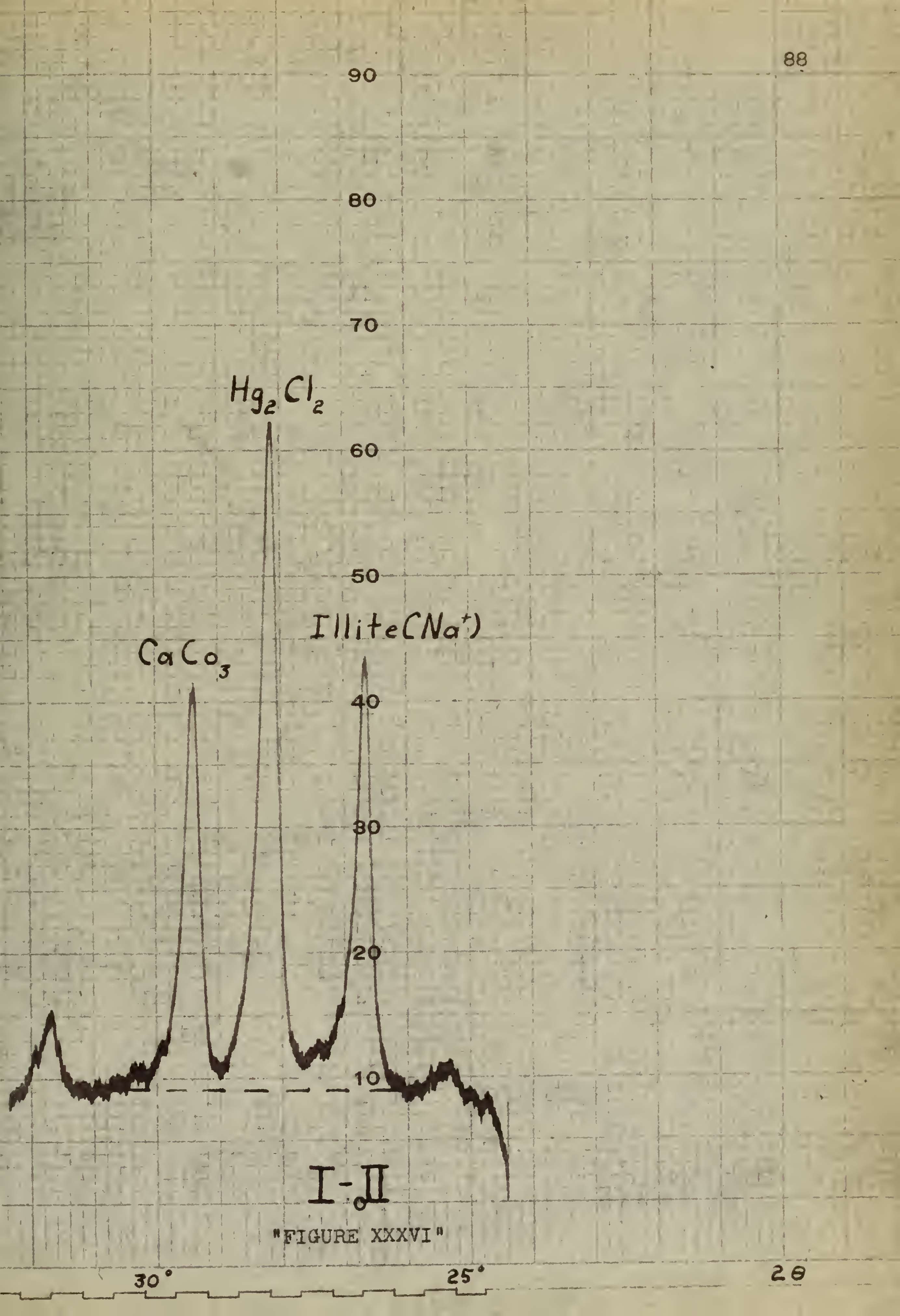
Mixtures:		Weight (grams) I-I	I-II	I-III	I-IV
Clay Mineral	- Illite (Na^+)	2.00	1.40	0.80	0.40
Diluent	- $CaCo_3$	0.00	0.60	1.20	1.60
Standard	- Hg_2Cl_2	1.00	1.00	1.00	1.00

Spectrometer Data

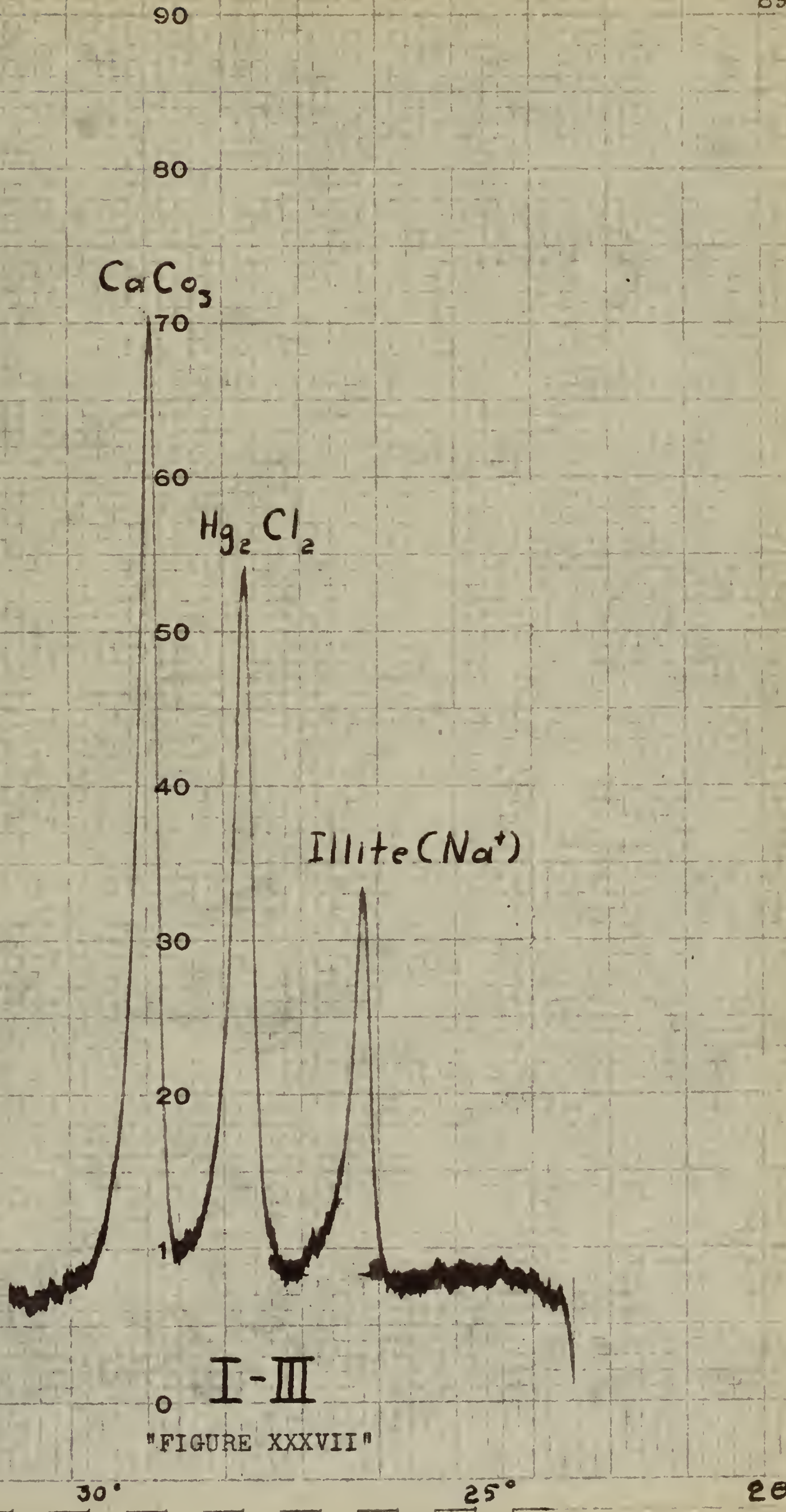
Same as Section I



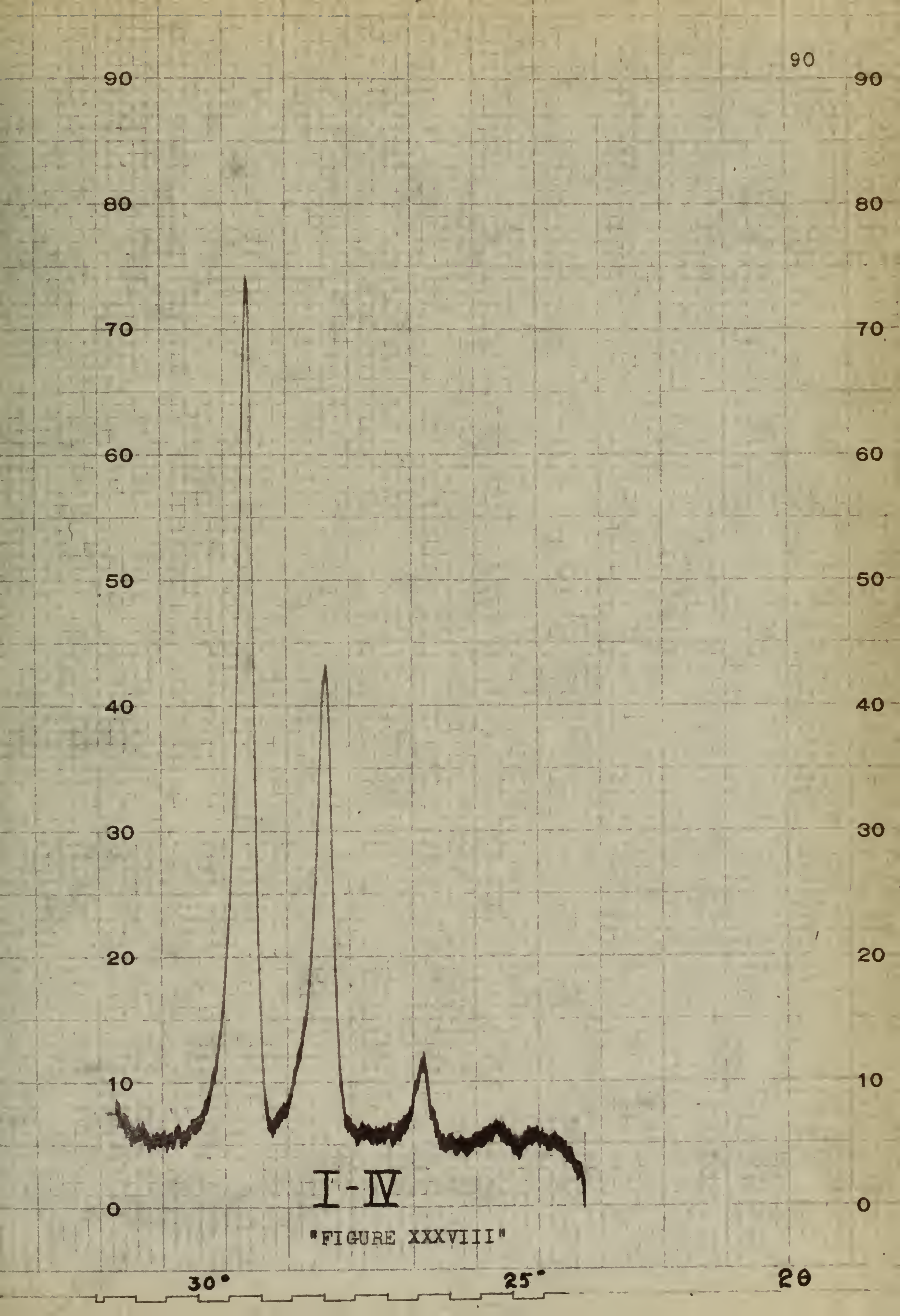
"FIGURE XXXV"



"FIGURE XXXVI"



"FIGURE XXXVII"



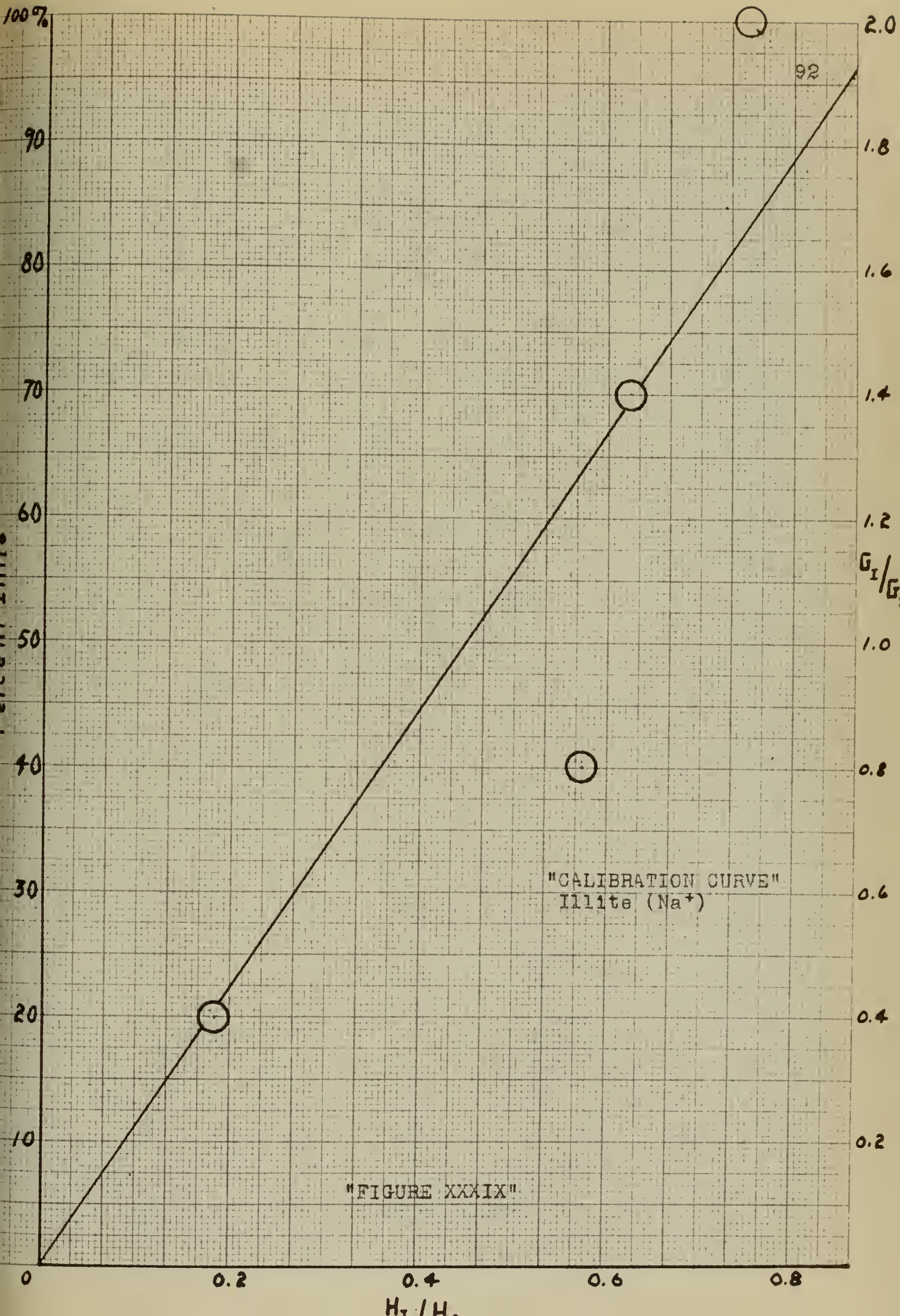
"FIGURE XXXVIII"

Table 6

DATA ACCUMULATION

Illite (Na^+) and Internal-Standard

	G_I/G_S		Height of Peak			Ave.	H_I/H_S
I-I	2.00	Illite	8.3	8.3	8.1	8.3	0.67
		Int. Std.	12.3	12.3	12.1	12.3	
I-II	1.40	Illite	6.9	6.6	6.8	6.7	0.63
		Int. Std.	10.7	10.7	10.7	10.7	
I-III	0.80	Illite	5.1	5.3	5.3	5.3	0.57
		Int. Std.	9.4	9.0	9.4	9.3	
I-IV	0.40	Illite	1.5	1.3	1.7	1.5	0.19
		Int. Std.	7.5	7.8	7.9	7.7	



92
100%
90
80
70
60
50
40
30
20
10
0
0.2
0.4
0.6
0.8
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
"CALIBRATION CURVE"
Illite (Na⁺)
"FIGURE XXXIX"

APPENDIX B

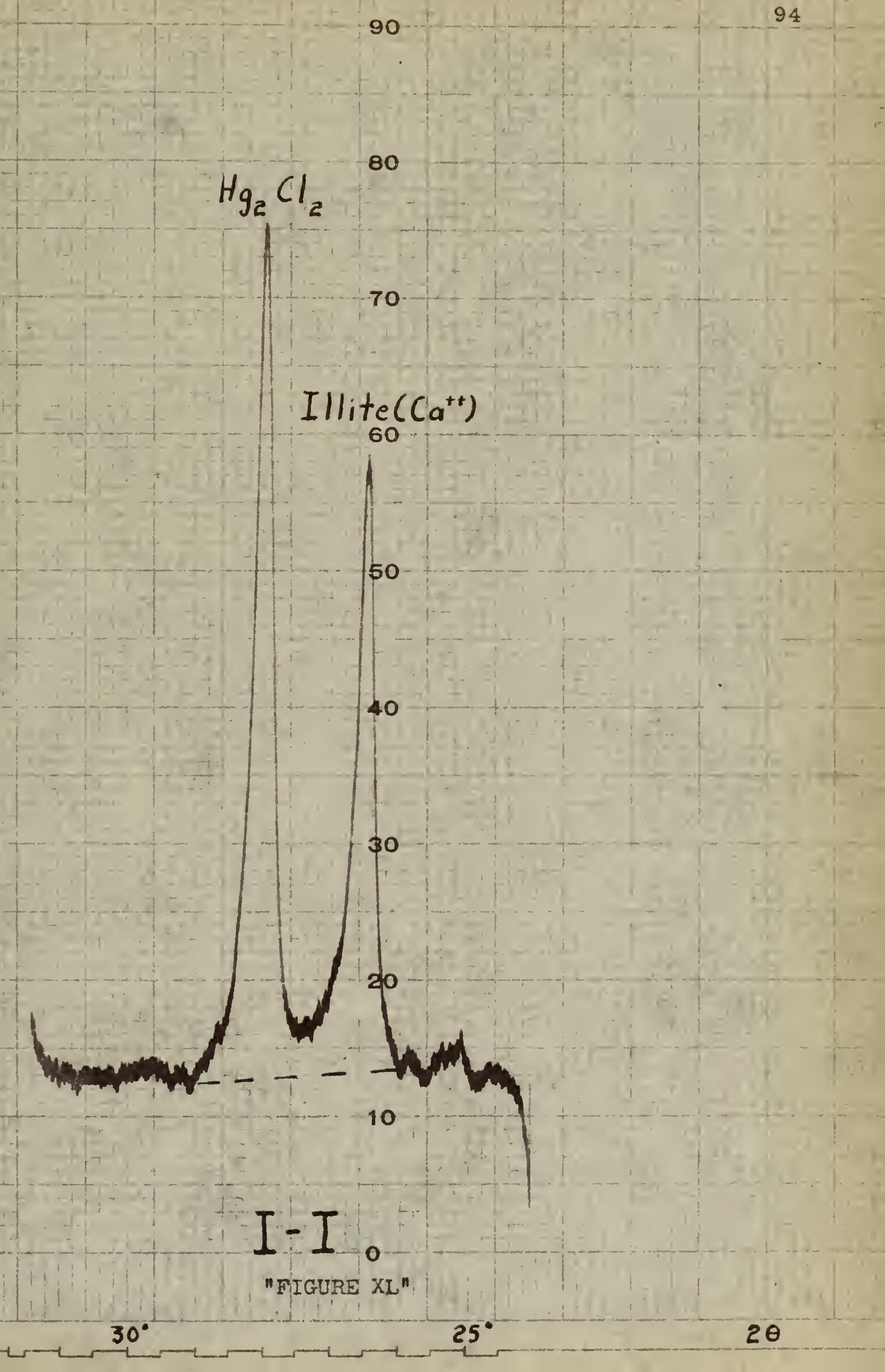
SECTION III

Ionic Saturation (Ca^{++})

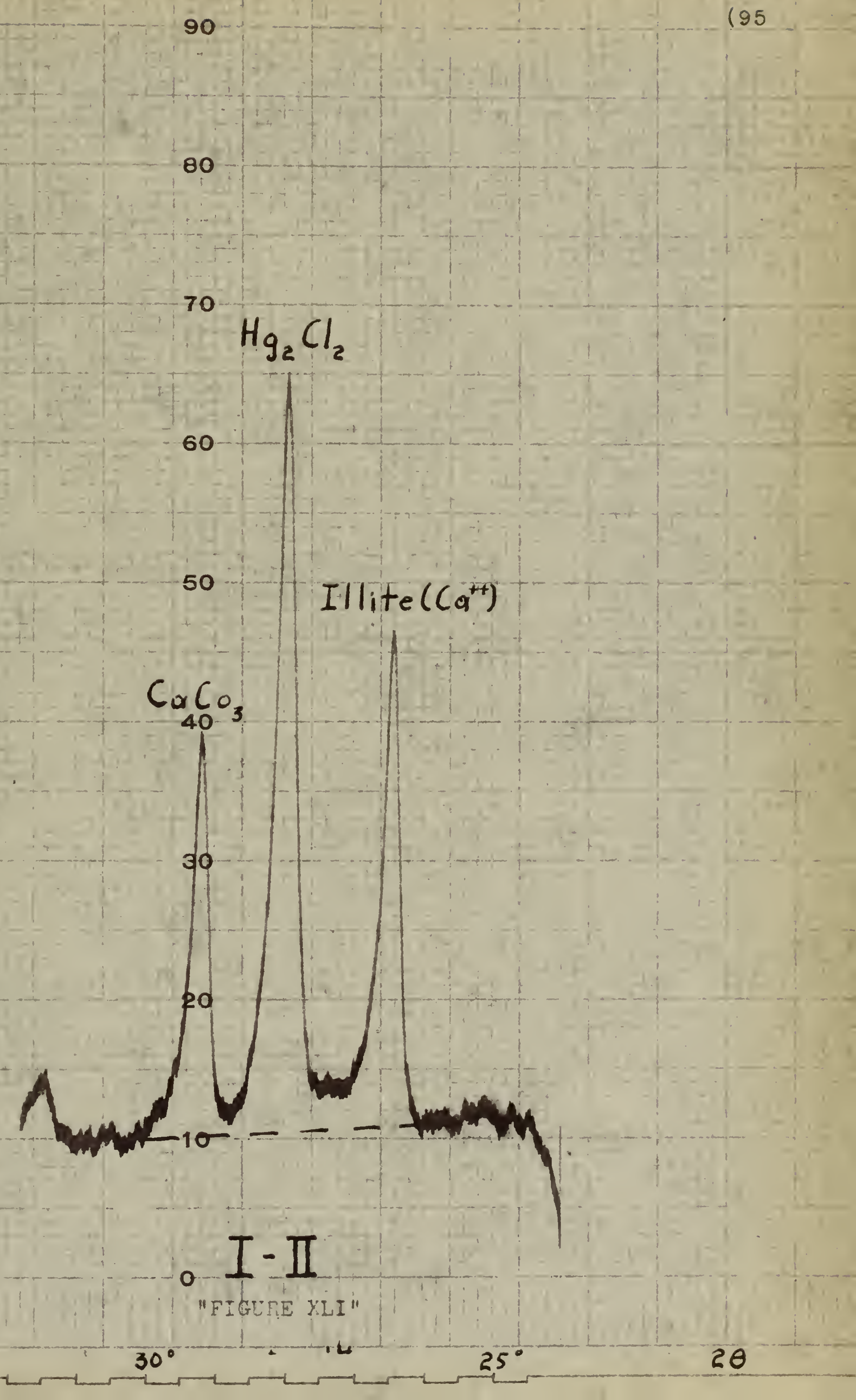
Mixtures:		Weight (grams)			
		I-I	I-II	I-III	I-IV
Clay Mineral	- Illite (Ca^{++})	2.00	1.40	0.80	0.40
Diluent	- $CaCo_3$	0.00	0.60	1.20	1.60
Standard	- Hg_2Cl_2	1.00	1.00	1.00	1.00

Spectrometer Data

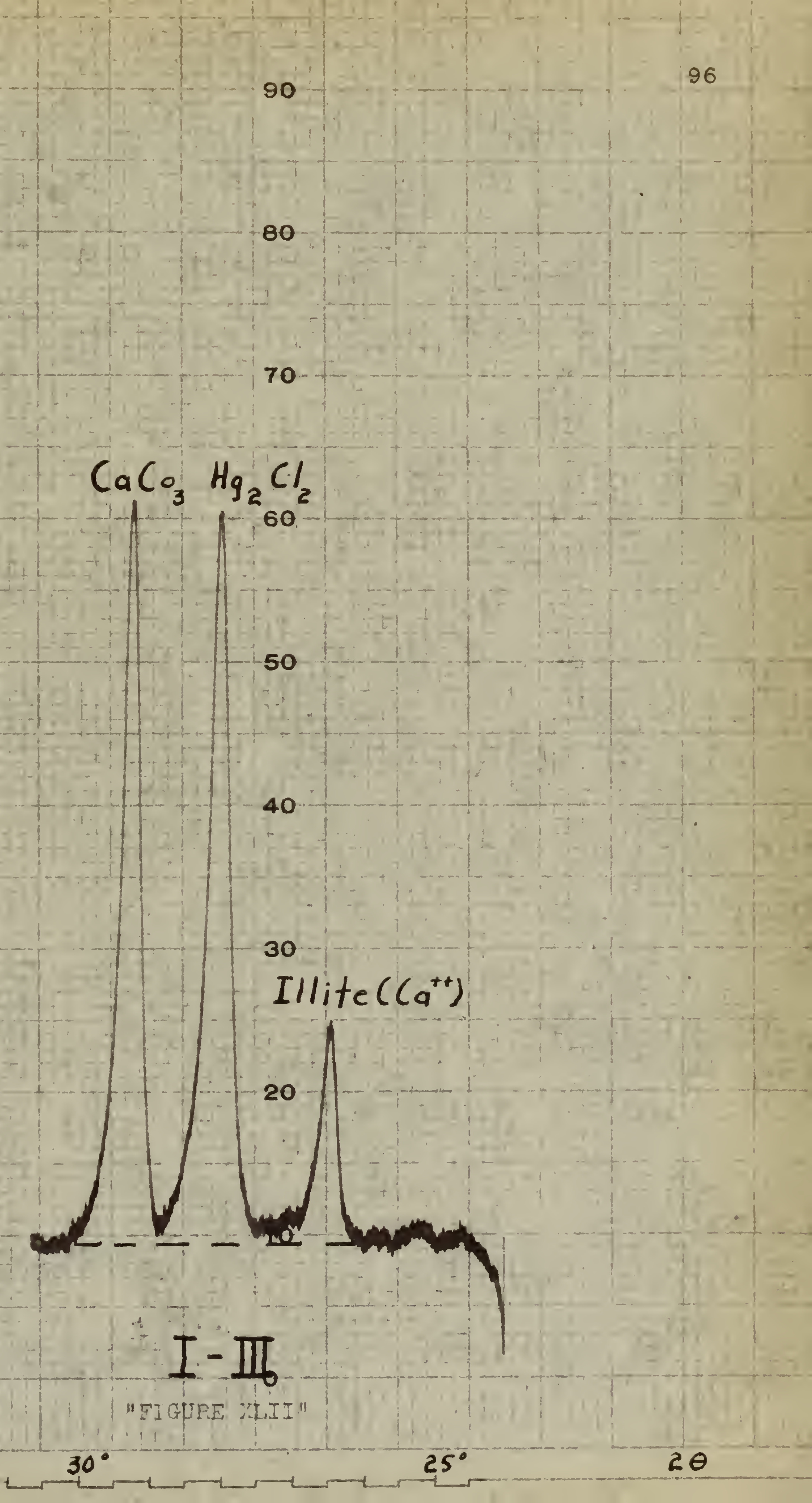
Same as Section I



"FIGURE XL"

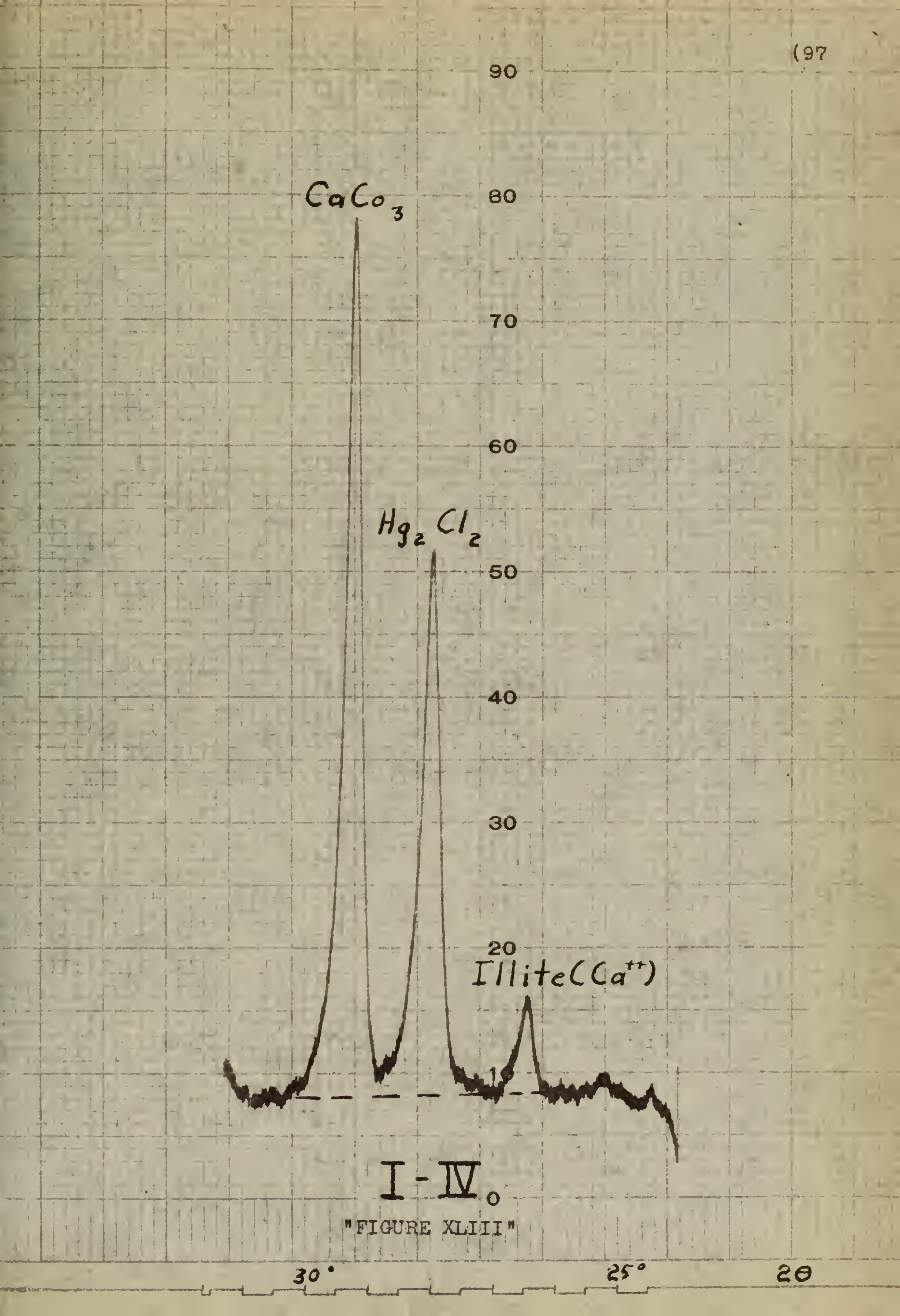


"FIGURE XLI"



I-III

"FIGURE XLII"



I - IV₀

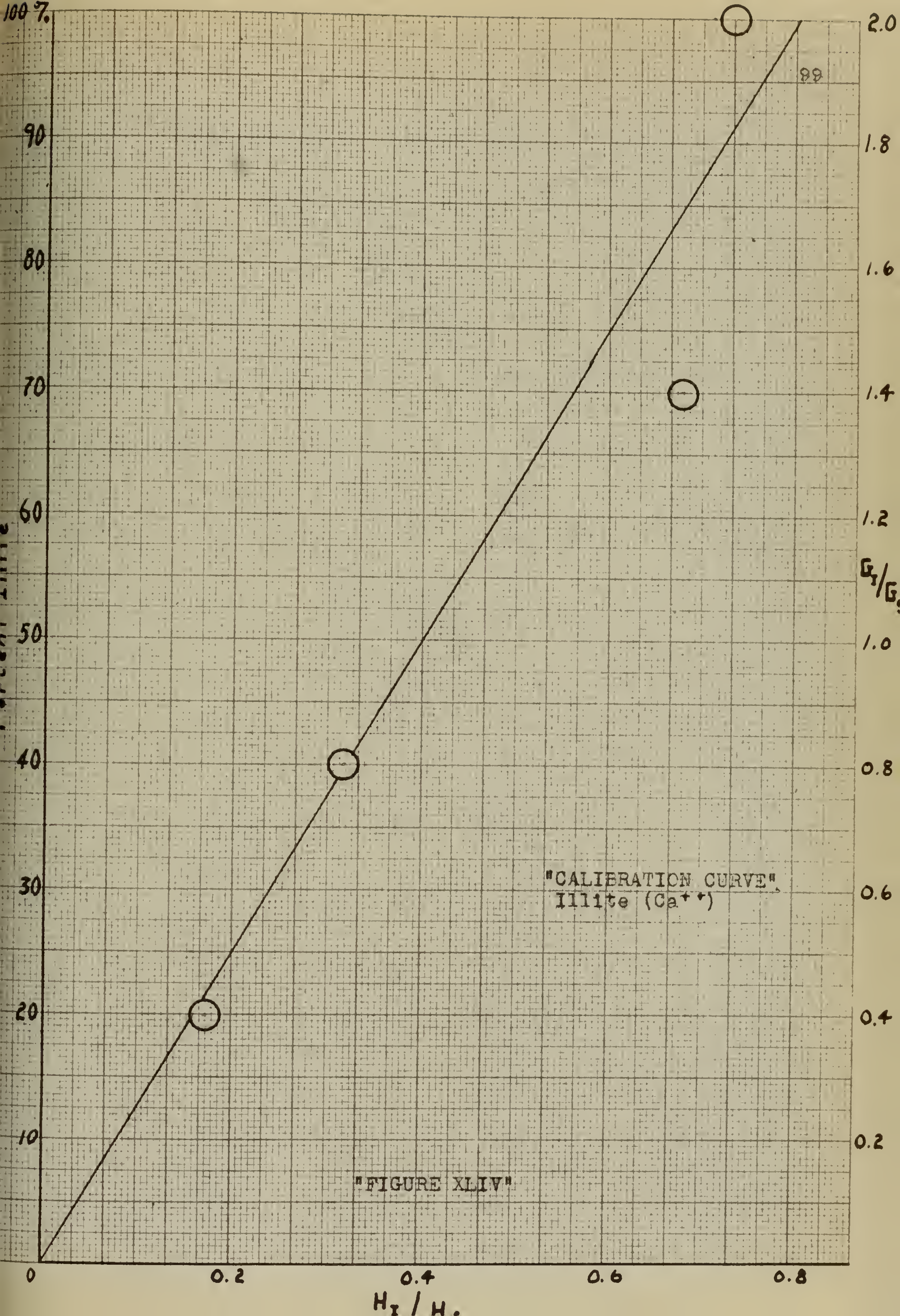
"FIGURE XLIII"

Table 7

DATA ACCUMULATION

Illite (Ca^{++}) and Internal-Standard

	G_I/G_s		Height of Peak			Ave.	H_I/H_s
I - I	2.00	Illite	8.5	8.7	9.0	8.7	0.71
		Int. Std.	12.3	11.8	12.5	12.2	
I - II	1.40	Illite	7.7	7.7	7.1	7.7	0.67
		Int. Std.	11.4	11.4	10.9	11.4	
I - III	0.80	Illite	3.0	3.3	3.1	3.2	0.31
		Int. Std.	10.4	10.1	10.2	10.2	
I - IV	0.40	Illite	1.7	1.7	1.5	1.7	0.18
		Int. Std.	9.2	9.5	9.0	9.3	



"CALIBRATION CURVE"
Illite (Ca^{++})

"FIGURE XLIV"

APPENDIX B

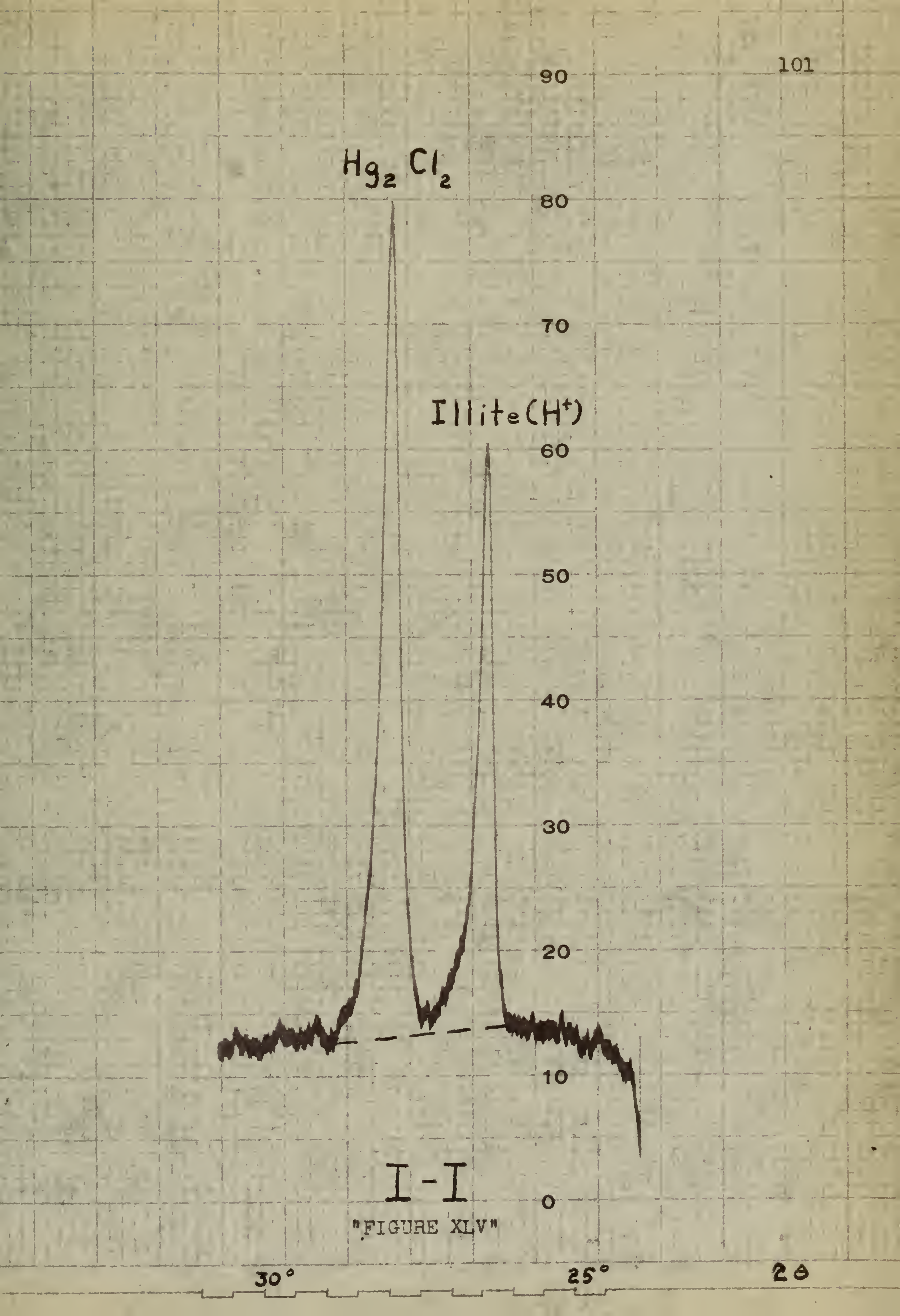
SECTION IV

Ionic Saturation (H^+)

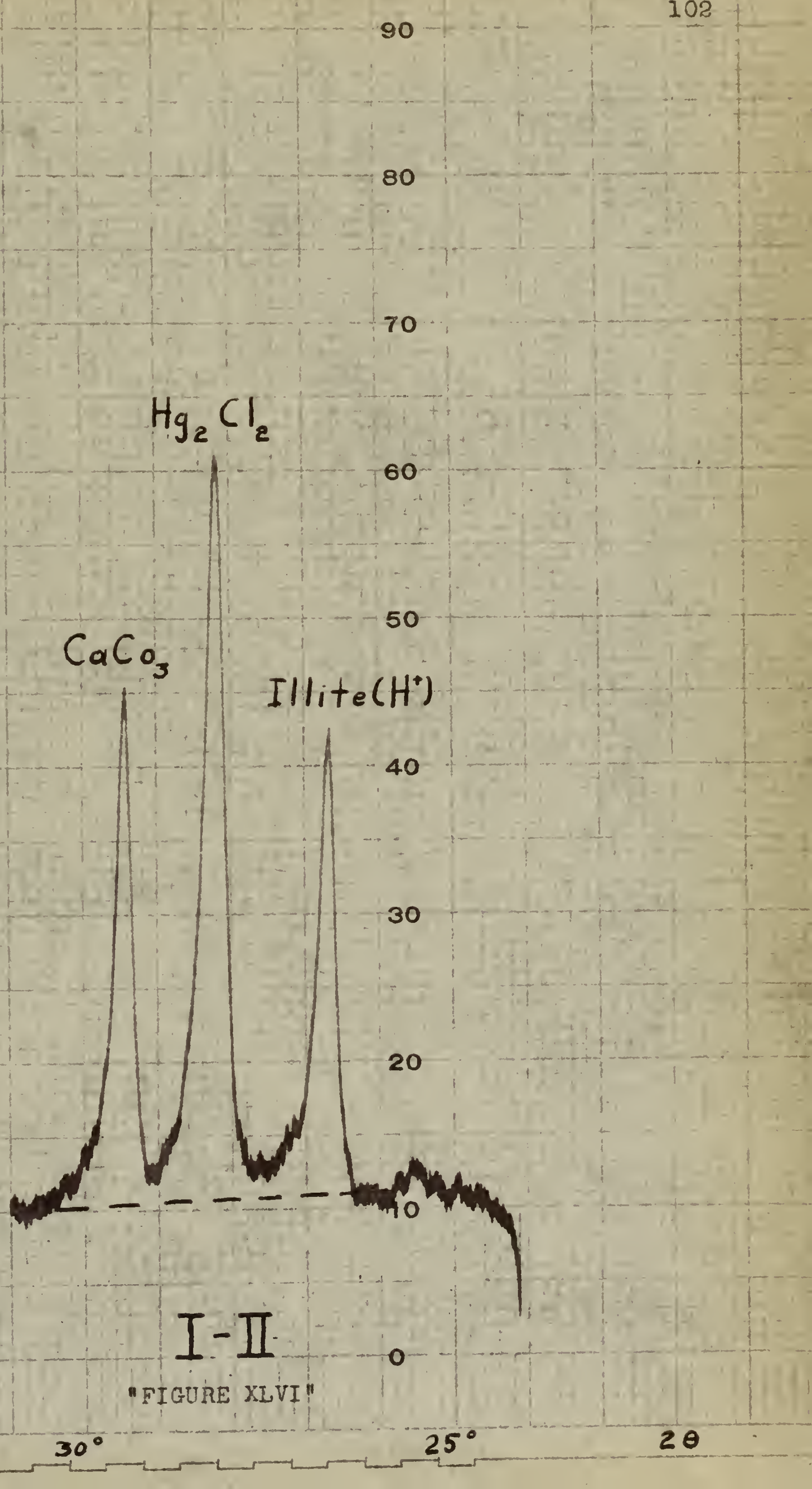
Mixtures:		Weight (grams)			
		I-I	I-II	I-III	I-IV
Clay Mineral	- Illite (H^+)	2.00	1.40	0.80	0.40
Diluent	- $CaCo_3$	0.00	0.60	1.20	1.60
Standard	- Hg_2Cl_2	1.00	1.00	1.00	1.00

Spectrometer Data

Same as Section I

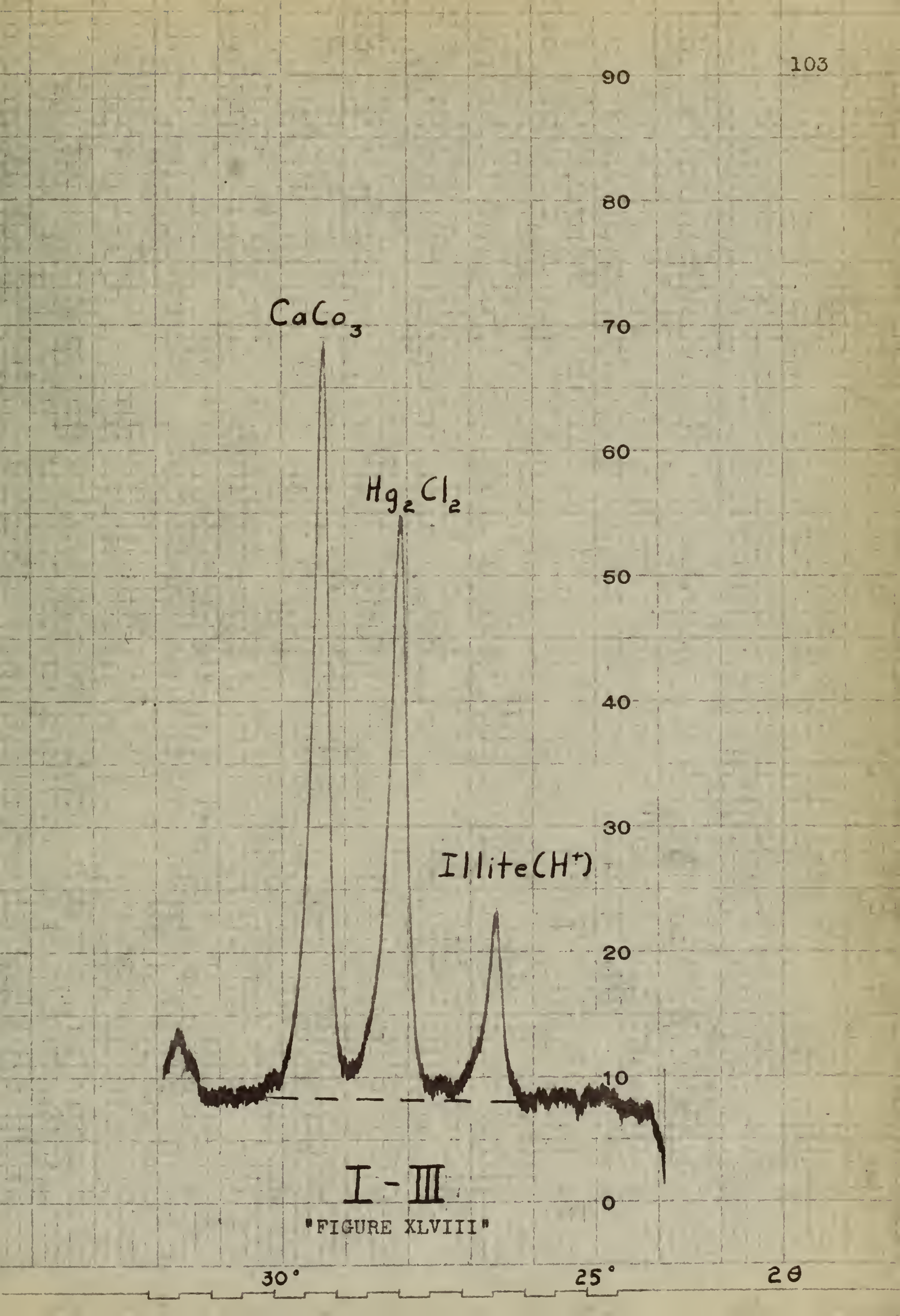


"FIGURE XLV"

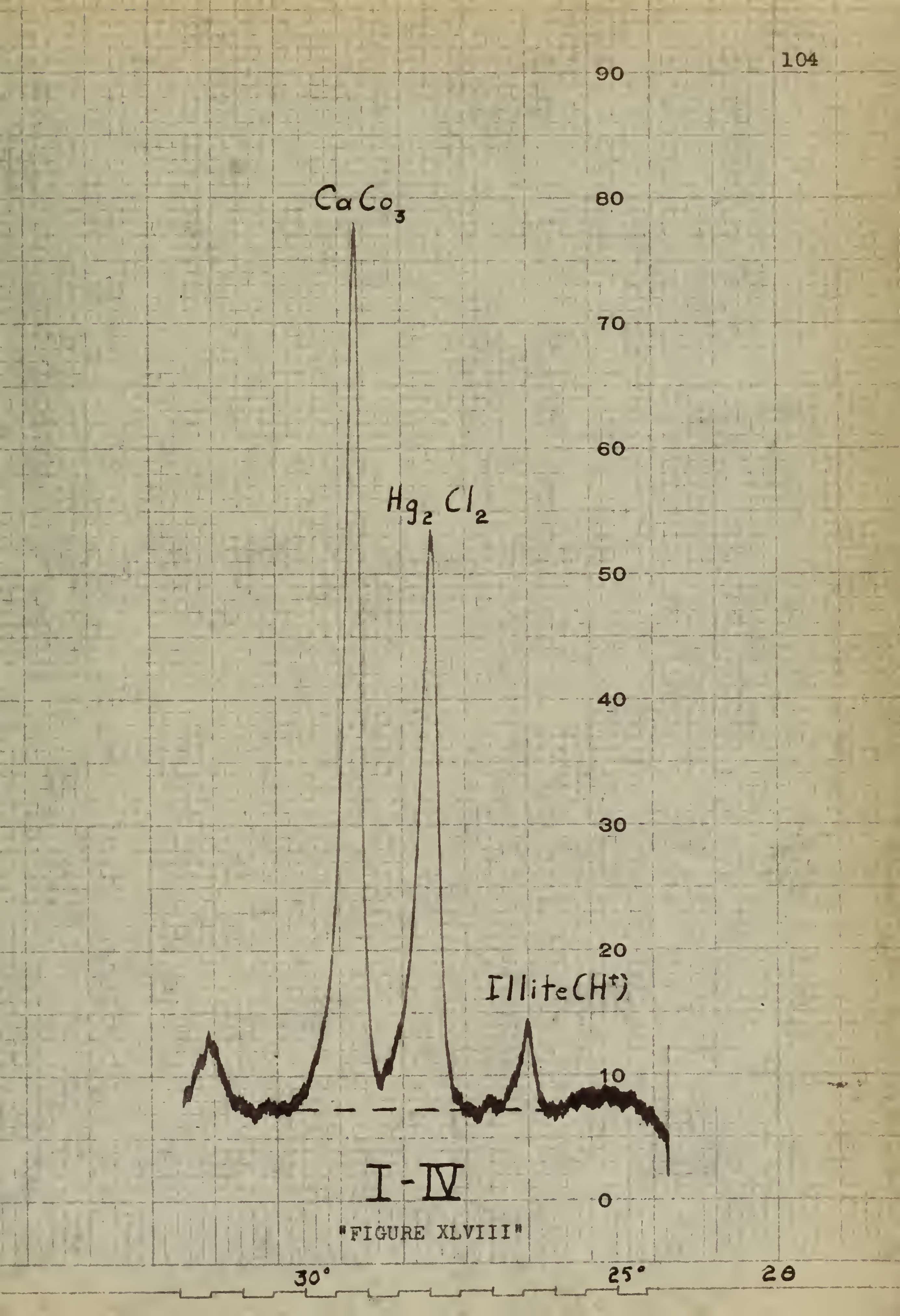


I-II

"FIGURE XLVI"



"FIGURE XLVIII"



"FIGURE XLVIII"

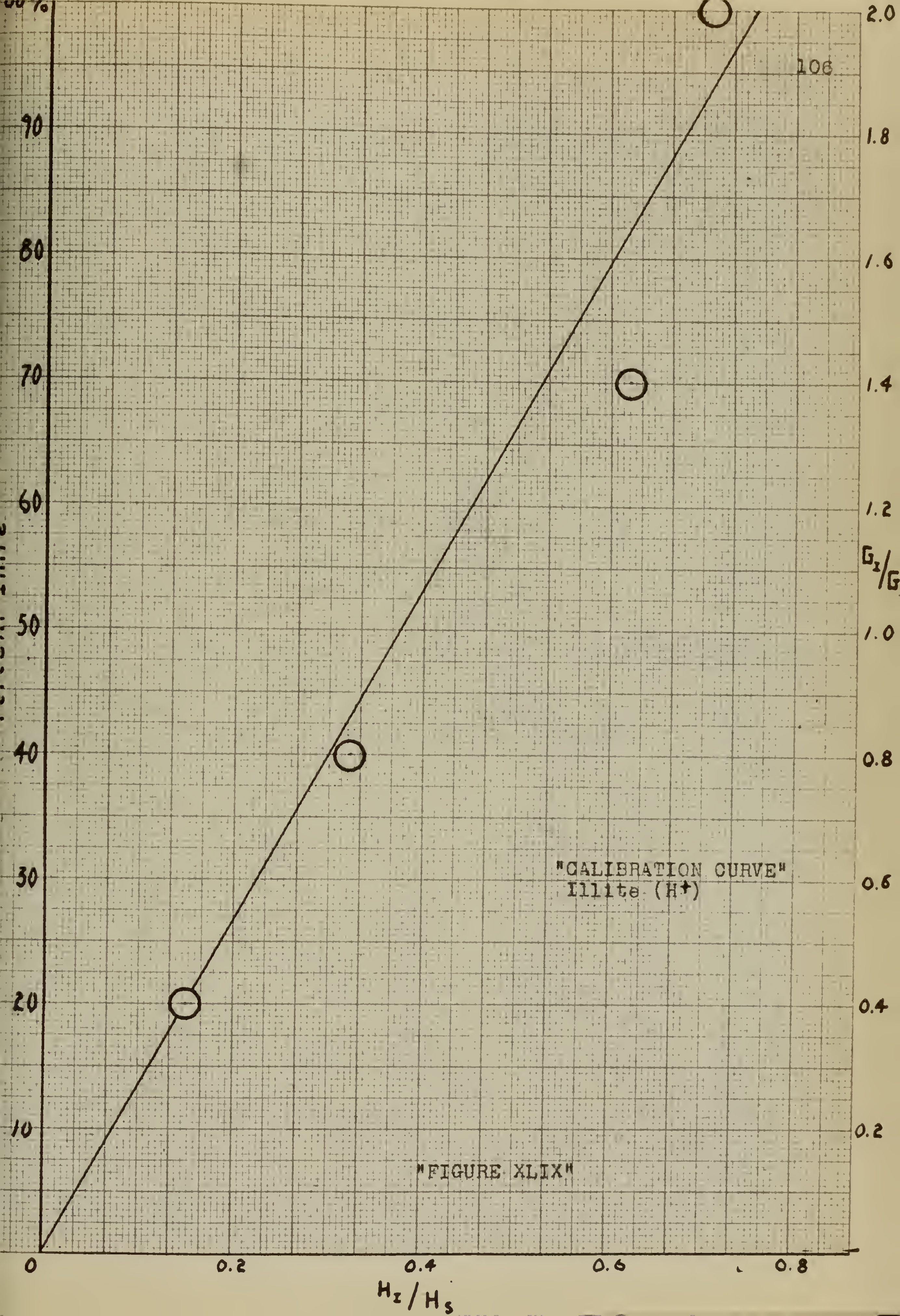
Table 8

DATA ACCUMULATION

Illite (H^+) and Internal-Standard

	G_I/G_s		Height at Peak			Ave.	H_I/H_s
I - I	2.00	Illite	9.3	9.6	9.5	9.4	0.70
		Int. Std.	13.4	13.3	13.5	13.3	
I - II	1.40	Illite	6.3	5.9	6.4	6.3	0.63
		Int. Std.	10.1	10.0	10.0	10.0	
I - III	0.80	Illite	3.1	[illegible]	[illegible]	3.0	0.33
		Int. Std.	9.3	9.1	9.0	9.1	
I - IV	0.40	Illite	1.4	1.4	1.6	1.4	0.15
		Int. Std.	9.0	9.3	9.5	9.3	

106



"FIGURE XLIX"

APPENDIX C

Diffraction Strip Charts and Calibration Curves for Montmorillonite with Internal Standard

Clay Mineral	-	Otay, California, Montmorillonite
Internal Standard	-	Zinc Sulfite
Diluent	-	Calcium Carbonate

APPENDIX C

SECTION I

Ionic Saturation (K^+)

Mixtures:		Weight (grams) M-I	M-II	M-III	M-IV
Clay Mineral	- Montmorillonite (K^+)	2.00	1.40	0.80	0.40
Diluent	- $CaCo_3$	0.00	0.60	1.20	1.60
Standard	- $Zn(S_2O_4)$	1.00	1.00	1.00	1.00

Spectrometer Data

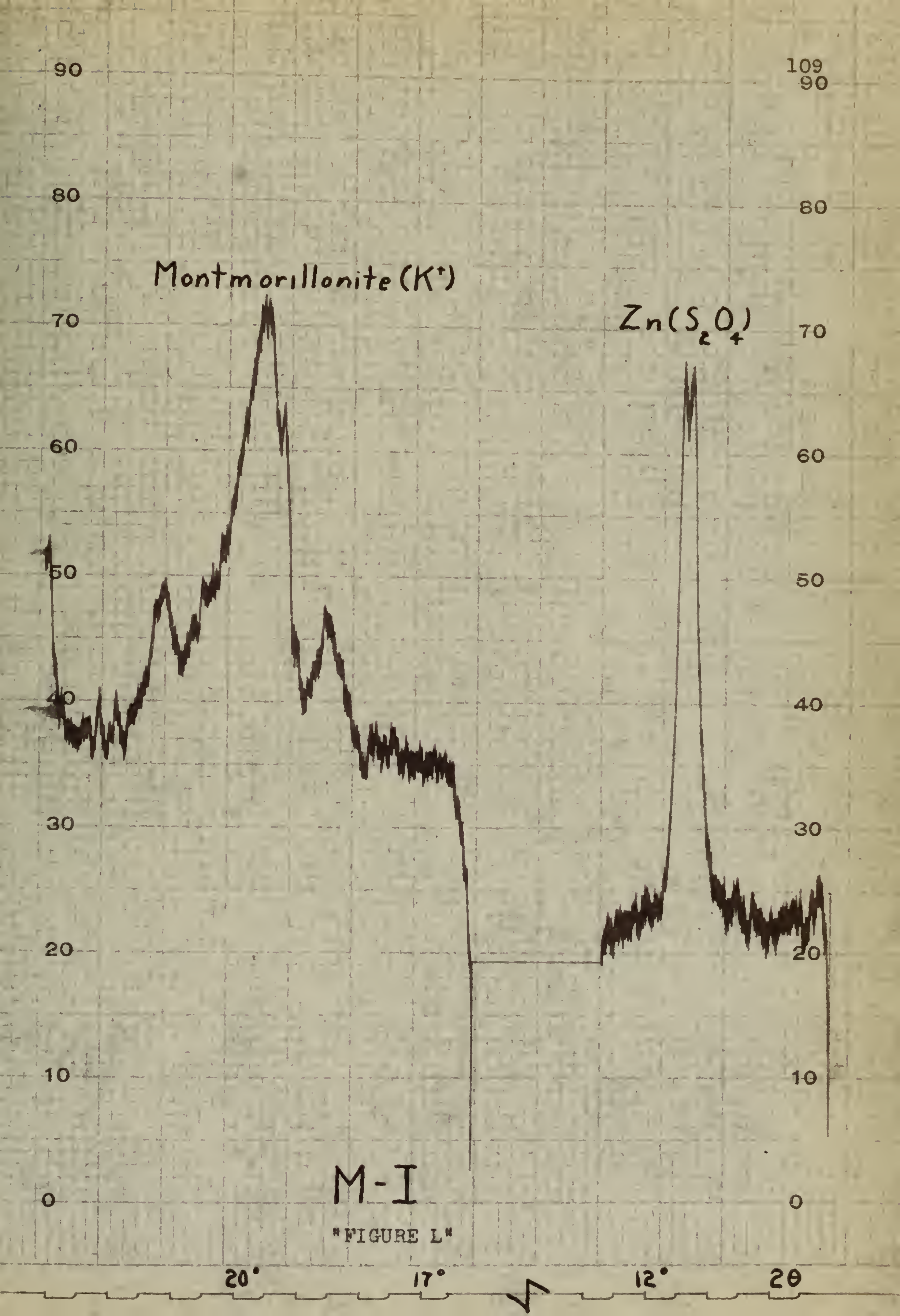
Radiation: Copper

Filter: Nickel

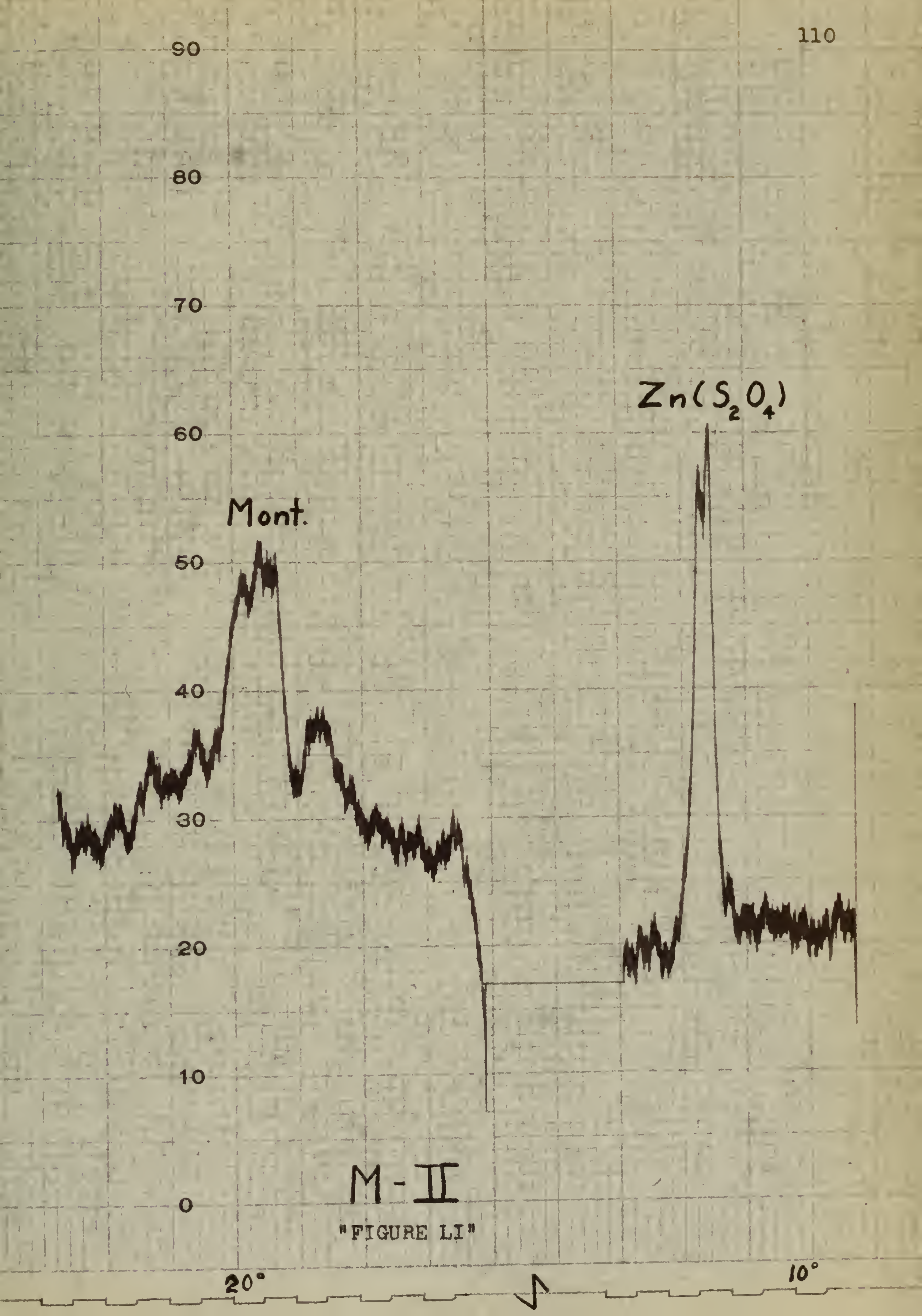
KVP: 70

Scanning Speed: $1^{o}(2\theta)$/MIN.

Rate Meter: Montmorillonite	Rate Meter: Zinc Sulfite
SF - 4	SF - 8
M - 0.6	M - 0.6
TC - 8	TC - 4

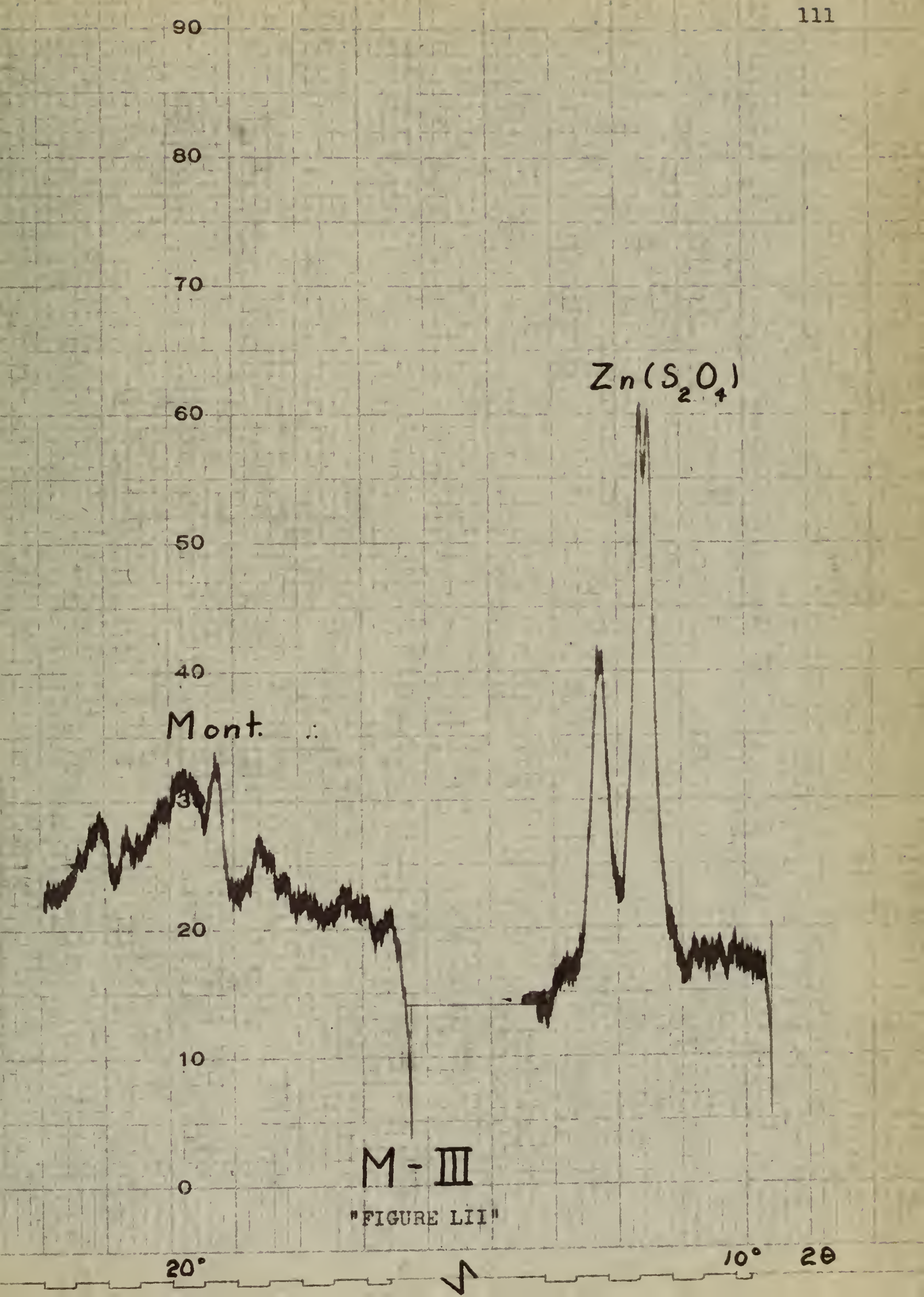

Montmorillonite (K+)
Zn(S2O4)
M-I
90
80
70
60
50
40
30
20
10
0
20°
17°
12°
2θ

"FIGURE L"

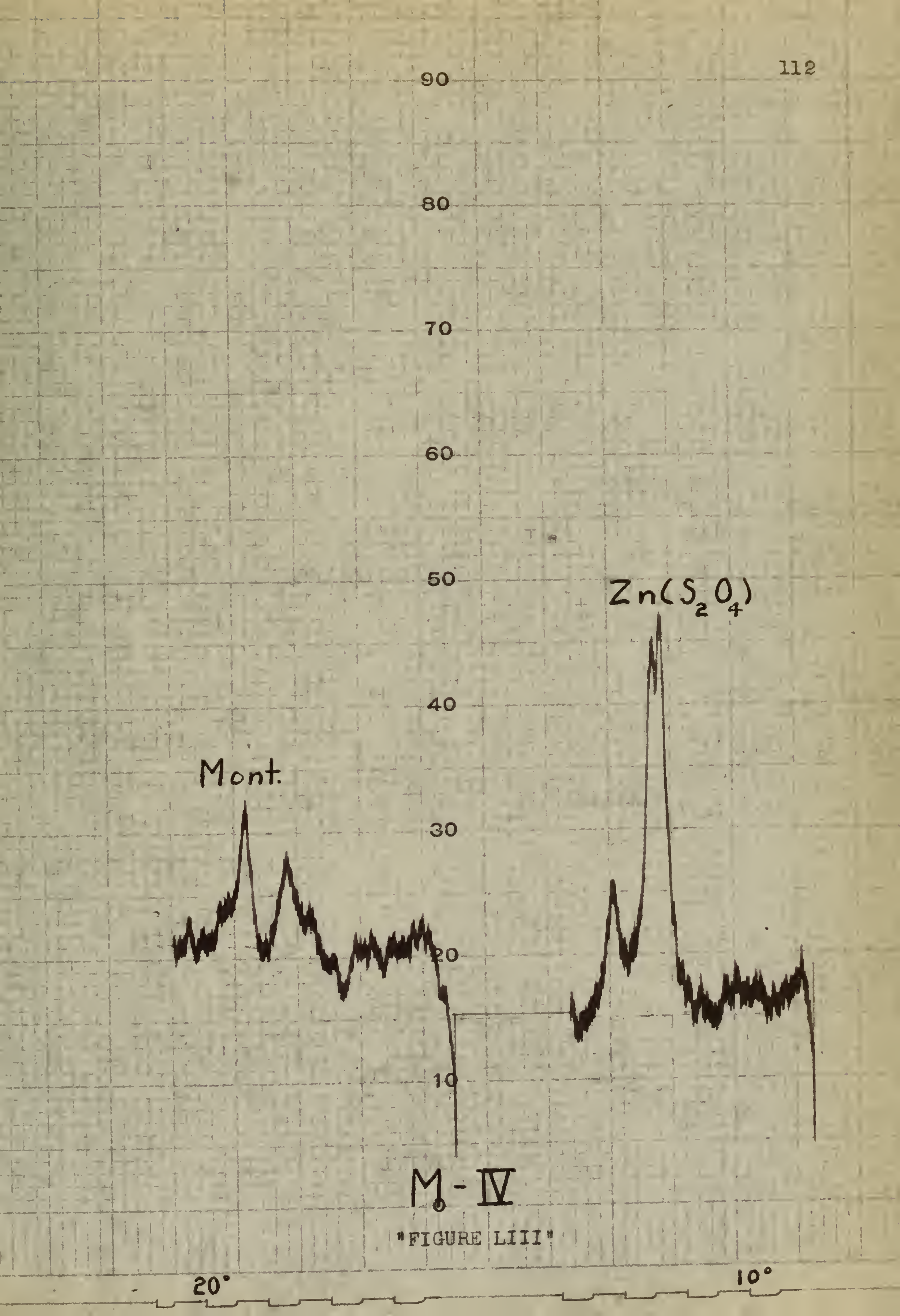


M-II

"FIGURE LI"



"FIGURE LII"



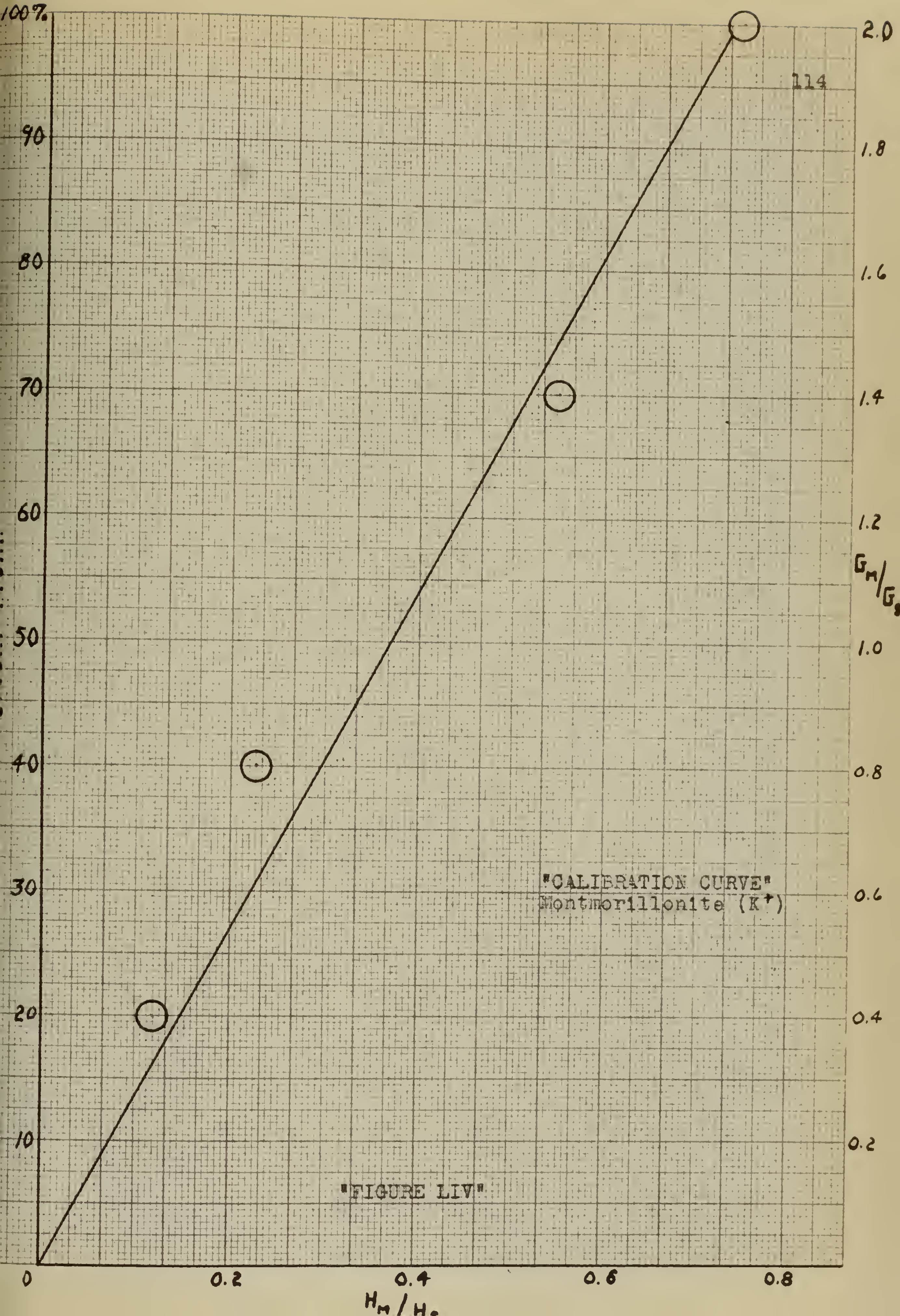
"FIGURE LIII"

Table 9

DATA ACCUMULATION

Montmorillonite (K^+) and Internal-Standard

	G_m/G_s		Height of Peak			Ave.	H_m/H_s
M-I	2.00	Mont.	7.2	6.9	6.9	6.9	0.74
		Int. Std.	9.0	9.4	9.3	9.3	
M-II	1.40	Mont.	3.8	4.7	4.0	4.0	0.55
		Int. Std.	8.0	7.5	7.[illegible]	7.3	
M-III	0.80	Mont.	1.9	2.0	2.0	2.0	0.23
		Int. Std.	8.7	8.8	8.5	8.6	
M-IV	0.40	Mont.	0.9	0.8	0.8	0.8	0.12
		Int. Std.	6.4	6.6	6.5	6.5	



100%
90
80
70
60
50
40
30
20
10
0
0.2
0.4
0.6
0.8
H_M / H_o
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
G_M/G_s
"CALIBRATION CURVE"
Montmorillonite (K^+)

"FIGURE LIV"

APPENDIX C

SECTION II

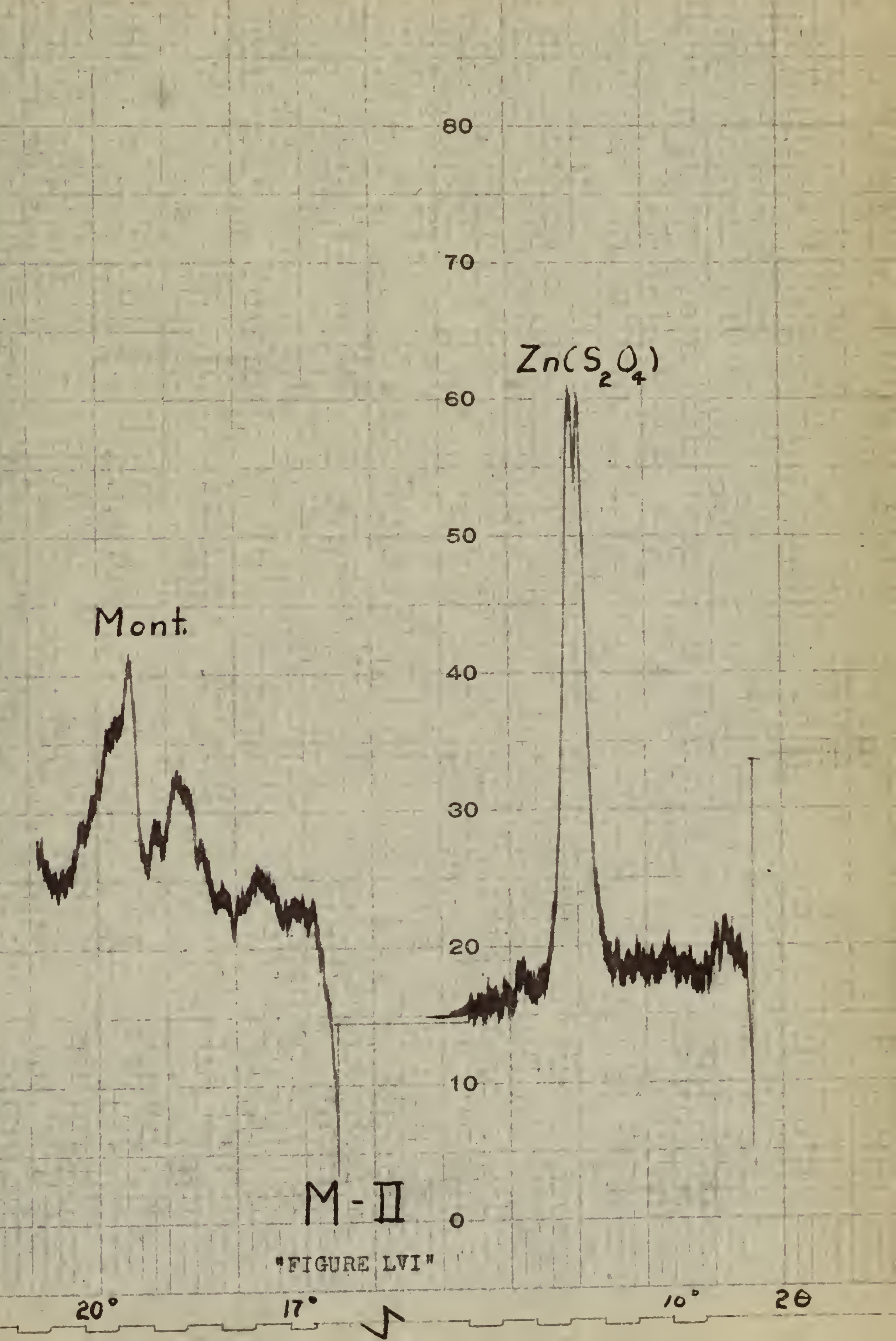
Ionic Saturation (Na^+)

Mixtures:		Weight (grams)			
		M-I	M-II	M-III	M-IV
Clay Mineral	- Montmorillonite (Na^+)	2.00	1.40	0.80	0.40
Diluent	- $CaCo_3$	0.00	0.60	1.20	1.60
Standard	- $Zn(S_2O_4)$	1.00	1.00	1.00	1.00

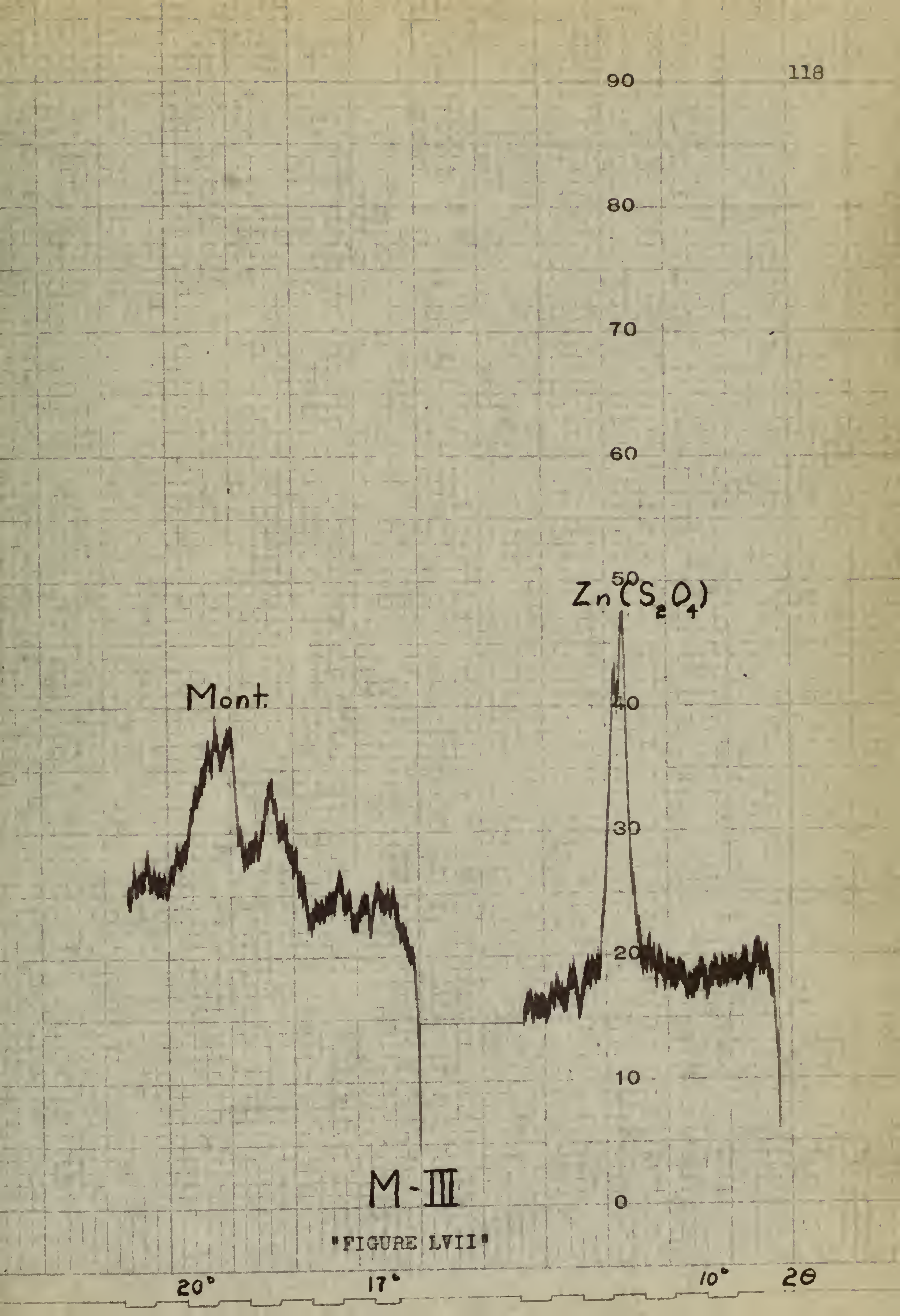
Spectrometer Data

Same as Section I

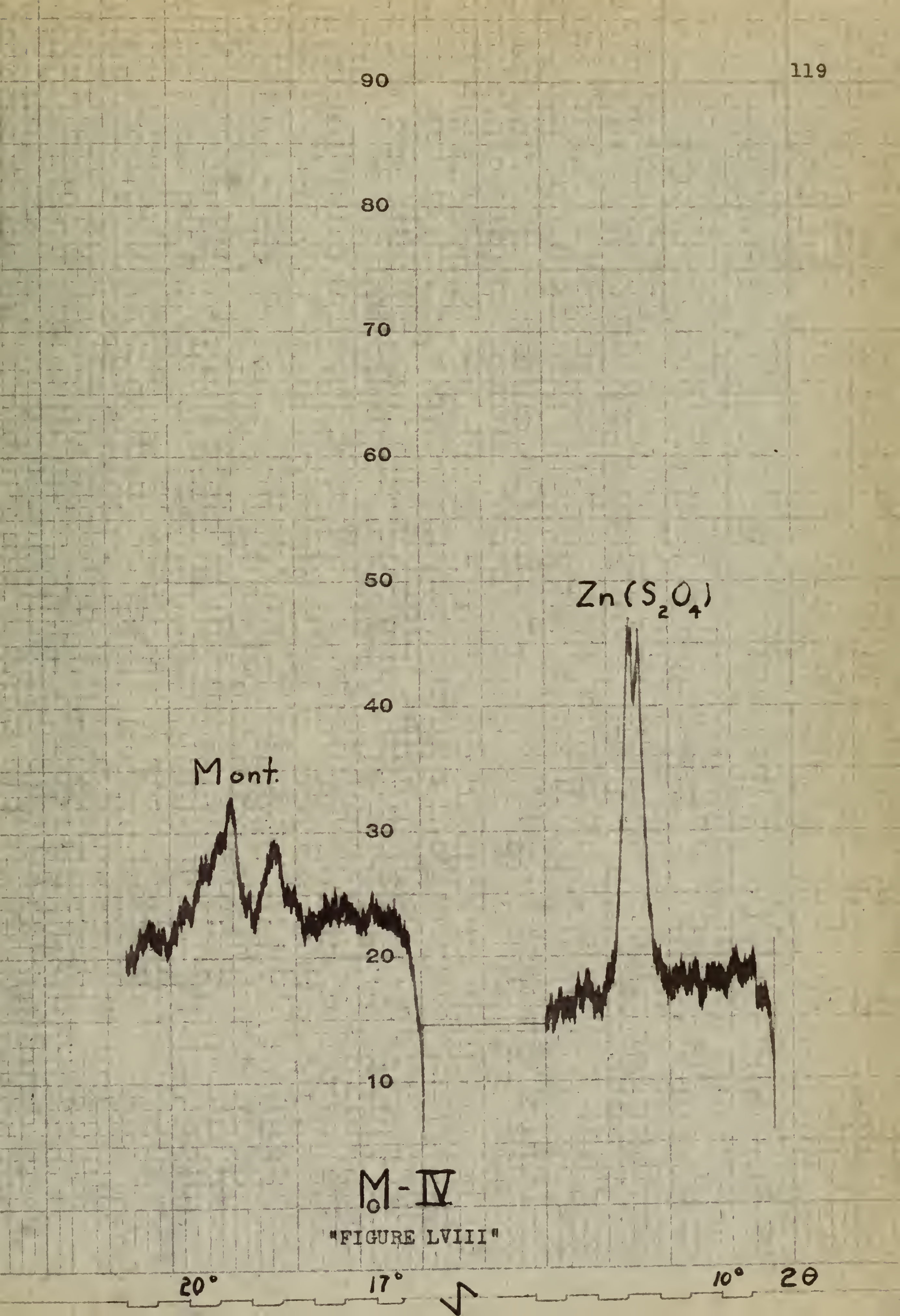
"FIGURE LV"



"FIGURE LVI"



"FIGURE LVII"



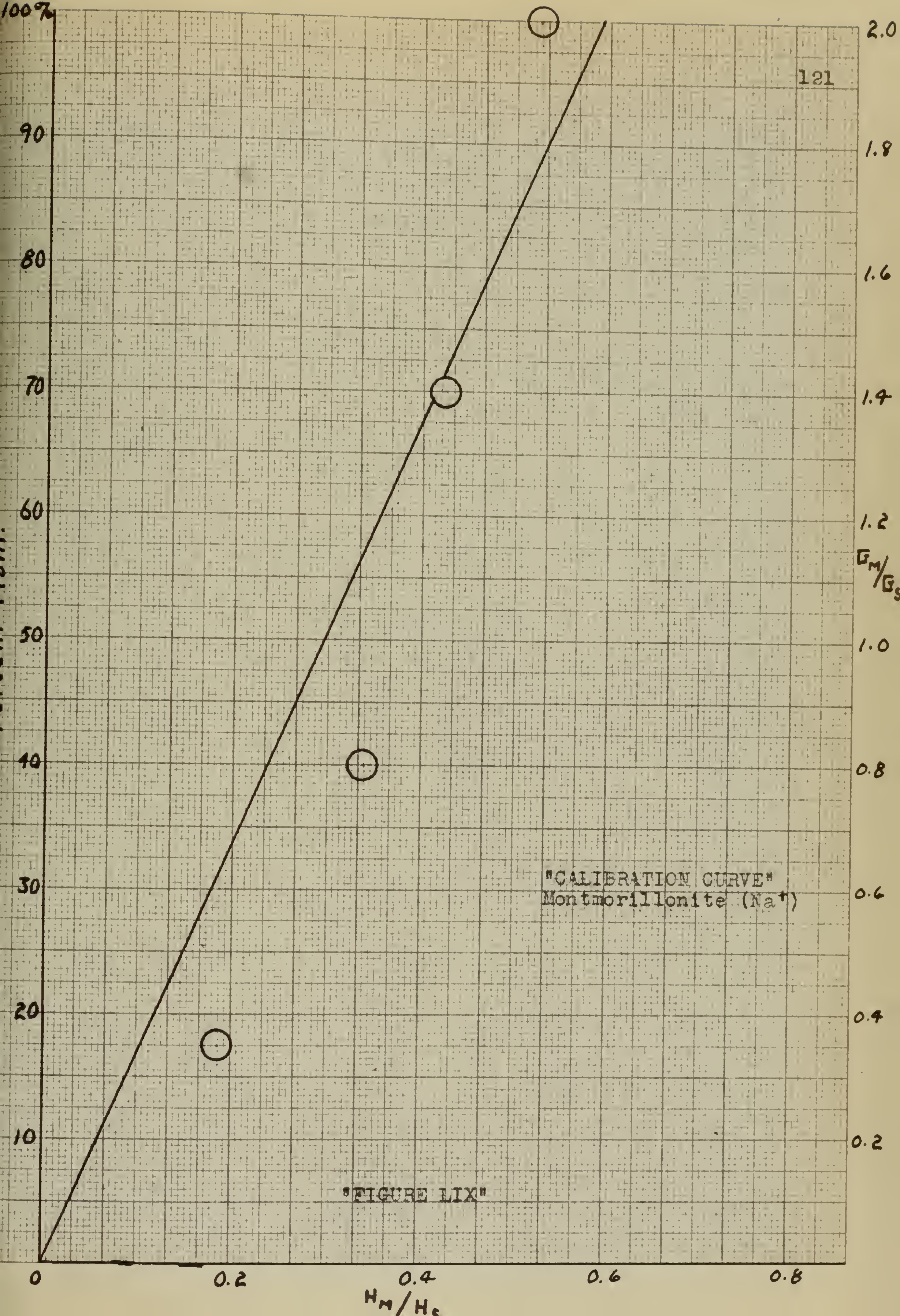
"FIGURE LVIII"

Table 10

DATA ACCUMULATION

Montmorillonite (Na^+) and Internal-Standard

	G_M/G_S		Height of Peak			Ave.	H_M/H_S
M-I	2.00	Mont.	6.1	6.6	5.9	6.3	0.52
		Int. Std.	12.1	11.9	12.4	12.1	
M-II	1.40	Mont.	3.6	3.9	3.5	3.6	0.42
		Int. Std.	8.5	8.7	8.6	8.6	
M-III	0.80	Mont.	2.0	2.1	1.9	2.0	0.34
		Int. Std.	5.7	6.2	5.8	5.9	
M-IV	0.40	Mont.	1.1	1.2	0.9	1.1	0.19
		Int. Std.	5.7	5.3	6.0	5.6	


100%
90
80
70
60
50
40
30
20
10
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
G_M/G_S
"CALIBRATION CURVE"
Montmorillonite (Na^+)
0
0.2
0.4
0.6
0.8
H_M/H_S

"FIGURE LIX"

APPENDIX C

SECTION III

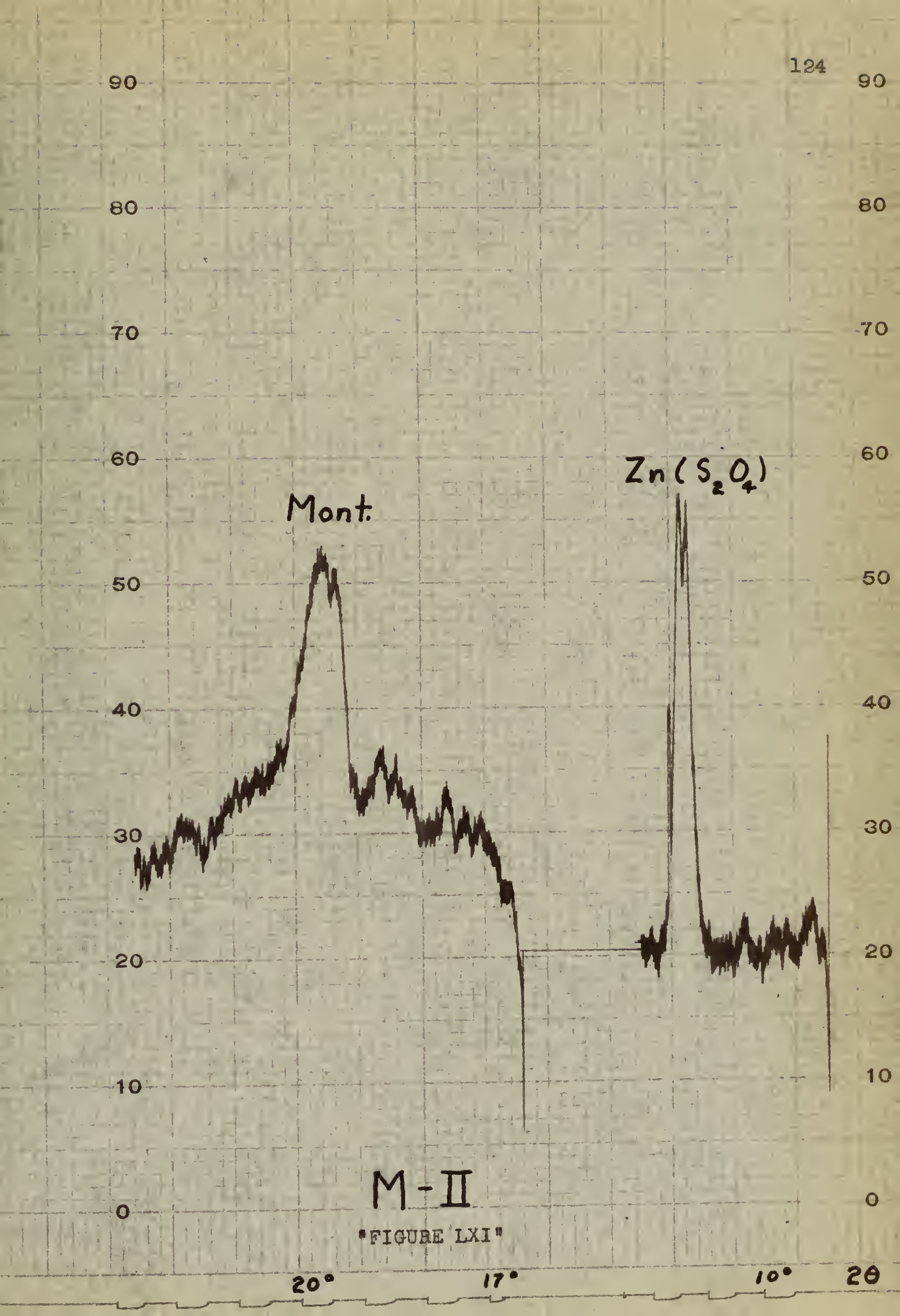
Ionic Saturation (Ca^{++})

Mixtures:		Weight (grams)			
		M-I	M-II	M-III	M-IV
Clay Mineral	- Montmorillonite (Ca^{++})	2.00	1.40	0.80	0.40
Diluent	- $CaCo_3$	0.00	0.60	1.20	1.60
Standard	- $Zn(S_2O_4)$	1.00	1.00	1.00	1.00

Spectrometer Data

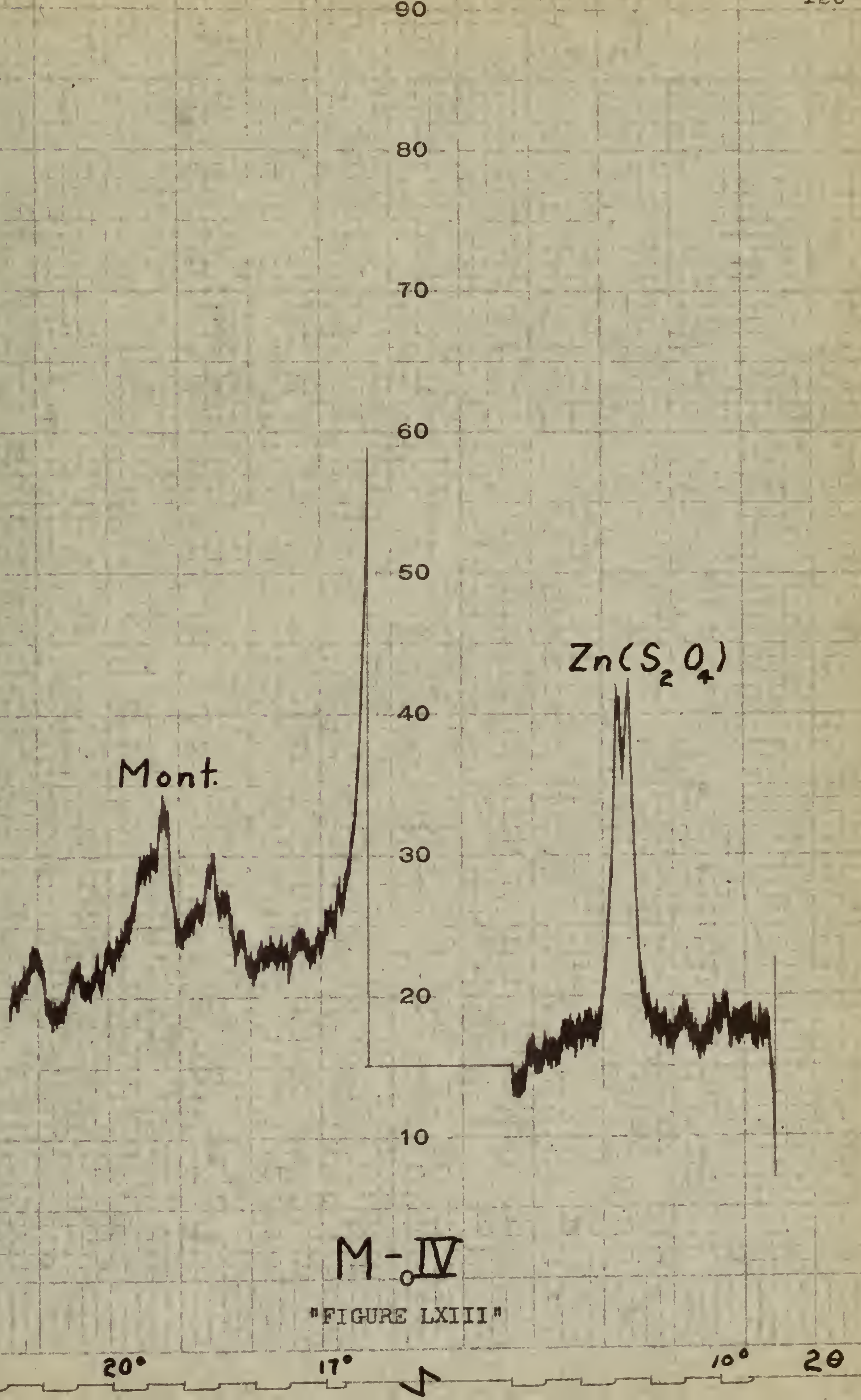
Same as Section I

"FIGURE LX"



"FIGURE LXI"

"FIGURE LXII"



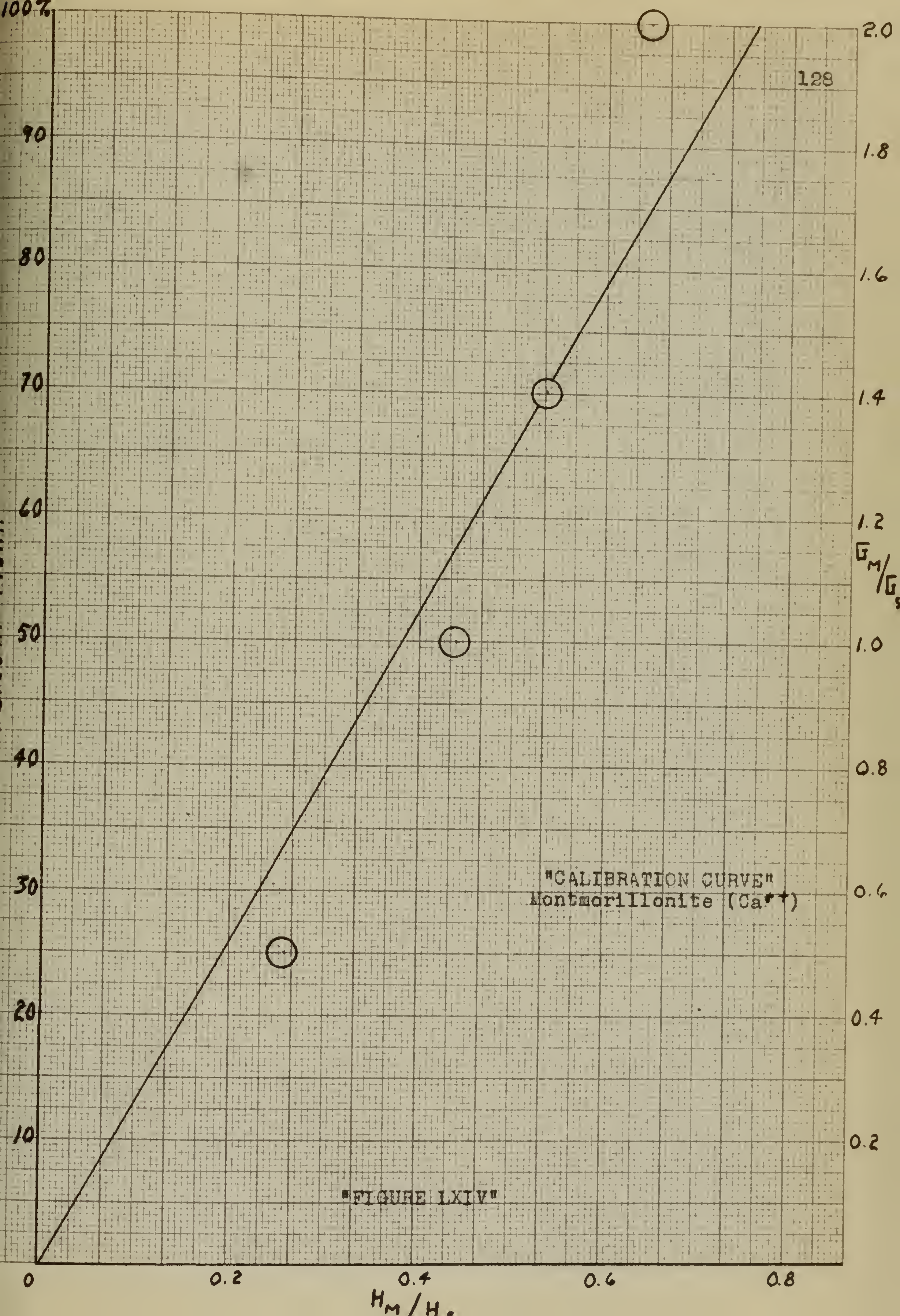
"FIGURE LXIII"

Table 11

DATA ACCUMULATION

Montmorillonite (Ca^{++}) and Internal-Standard

	G_M/G_S		Height of Peak			Ave.	H_M/H_S
M-I	2.00	Mont.	7.0	7.2	7.4	7.3	0.64
		Int. Std.	11.4	12.2	11.4	11.4	
M-II	1.40	Mont.	3.7	4.0	4.2	3.9	0.54
		Int. Std.	7.4	7.0	7.2	7.2	
M-III	0.80	Mont.	3.1	3.4	3.5	3.3	0.44
		Int. Std.	7.7	7.4	7.3	7.5	
M-IV	0.40	Mont.	1.2	1.2	1.4	1.4	0.26
		Int. Std.	5.0	5.4	5.2	5.3	


100%
90
80
70
60
50
40
30
20
10
0
0.2
0.4
0.6
0.8
H_M / H_s
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
G_M / G_s
"CALIBRATION CURVE"
Montmorillonite (Ca^{++})

"FIGURE LXIV"

APPENDIX C

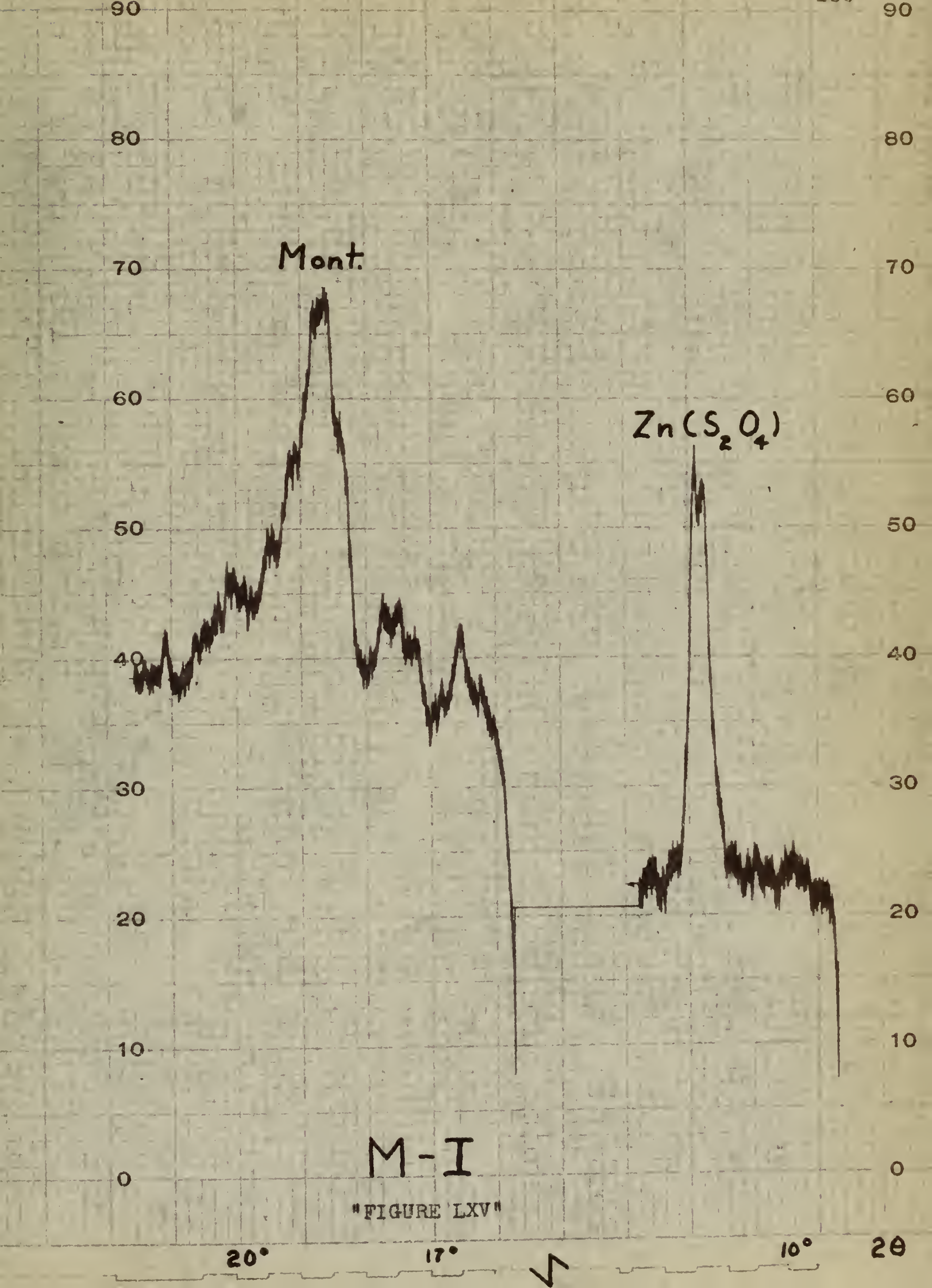
SECTION IV

Ionic Saturation (H^+)

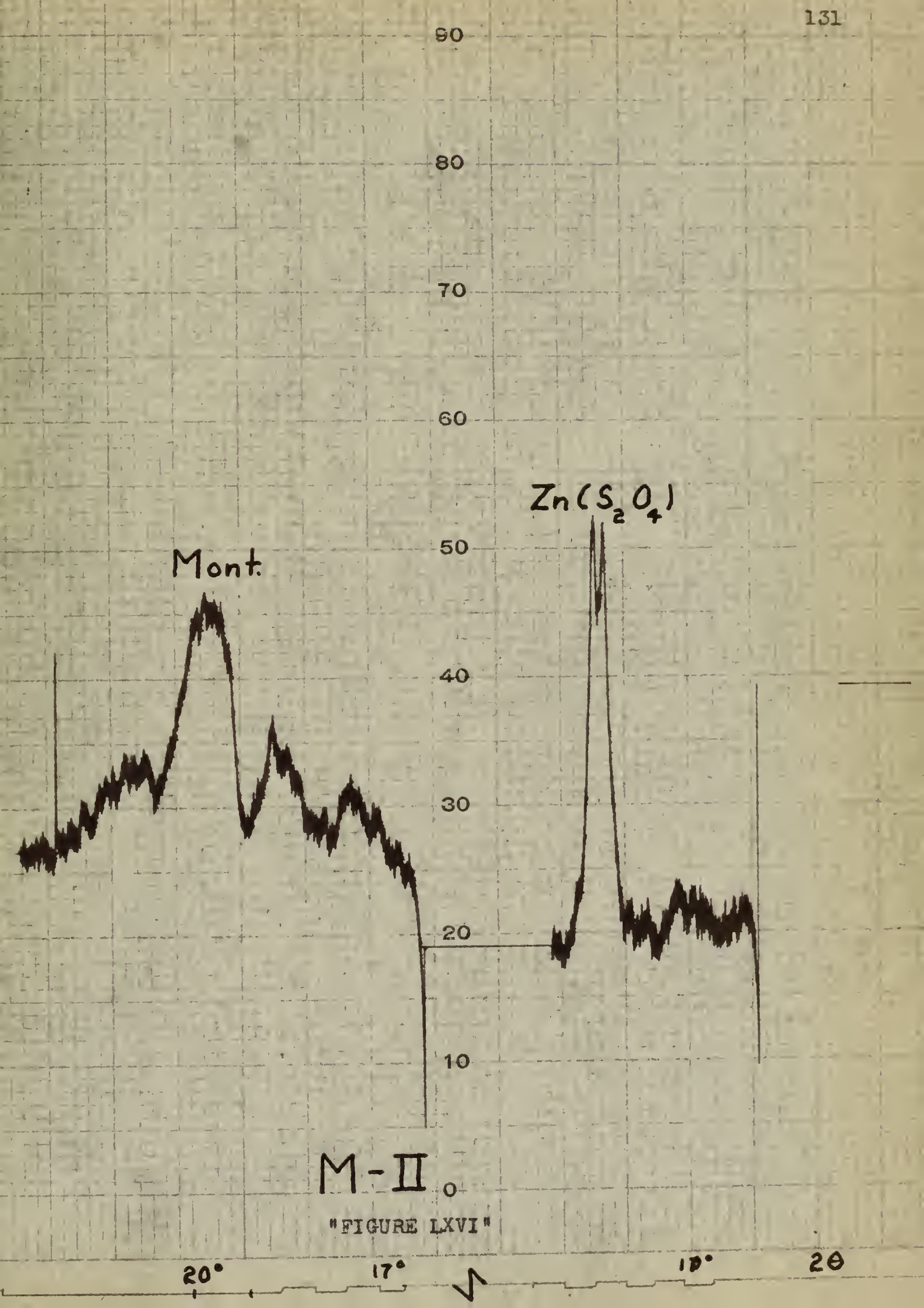
Mixtures:		Weight (grams)			
		M-I	M-II	M-III	M-IV
Clay Mineral	- Montmorillonite (H^+)	2.00	1.40	0.80	0.40
Diluent	- $CaCo_3$	0.00	0.60	1.20	1.60
Standard	- $Zn(S_2O_4)$	1.00	1.00	1.00	1.00

Spectrometer Data

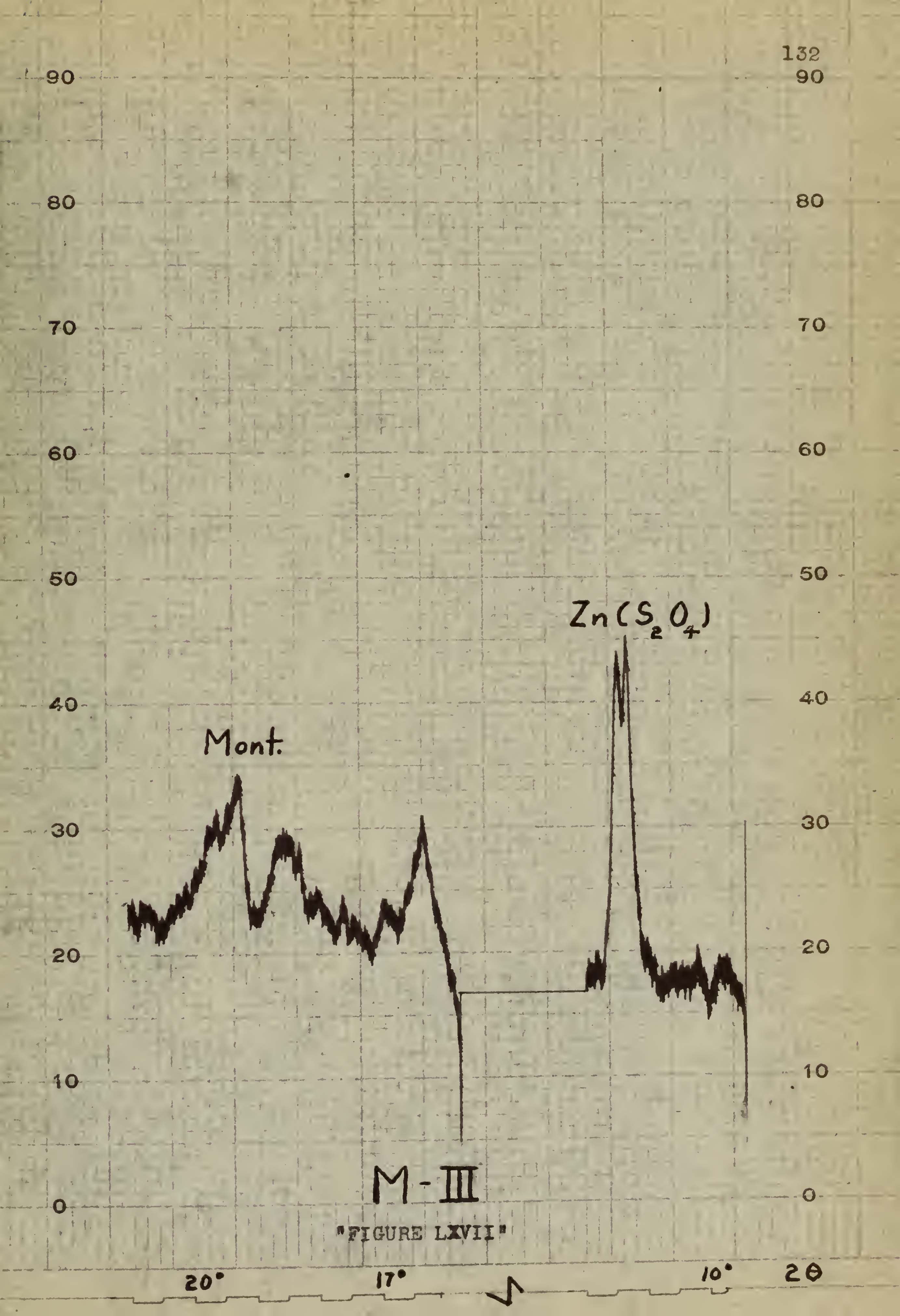
Same as Section I



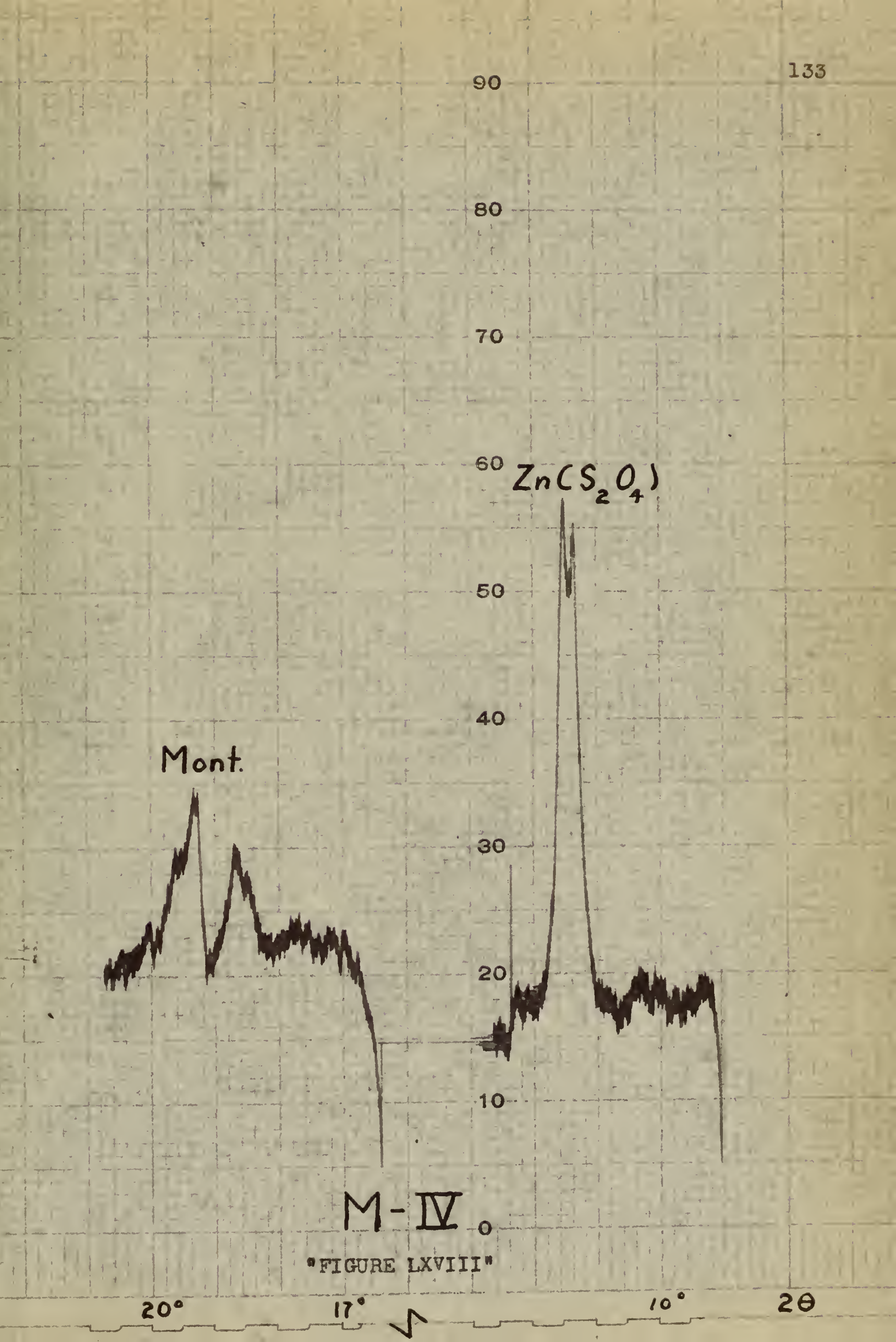
"FIGURE LXV"



"FIGURE LXVI"



"FIGURE LXVII"



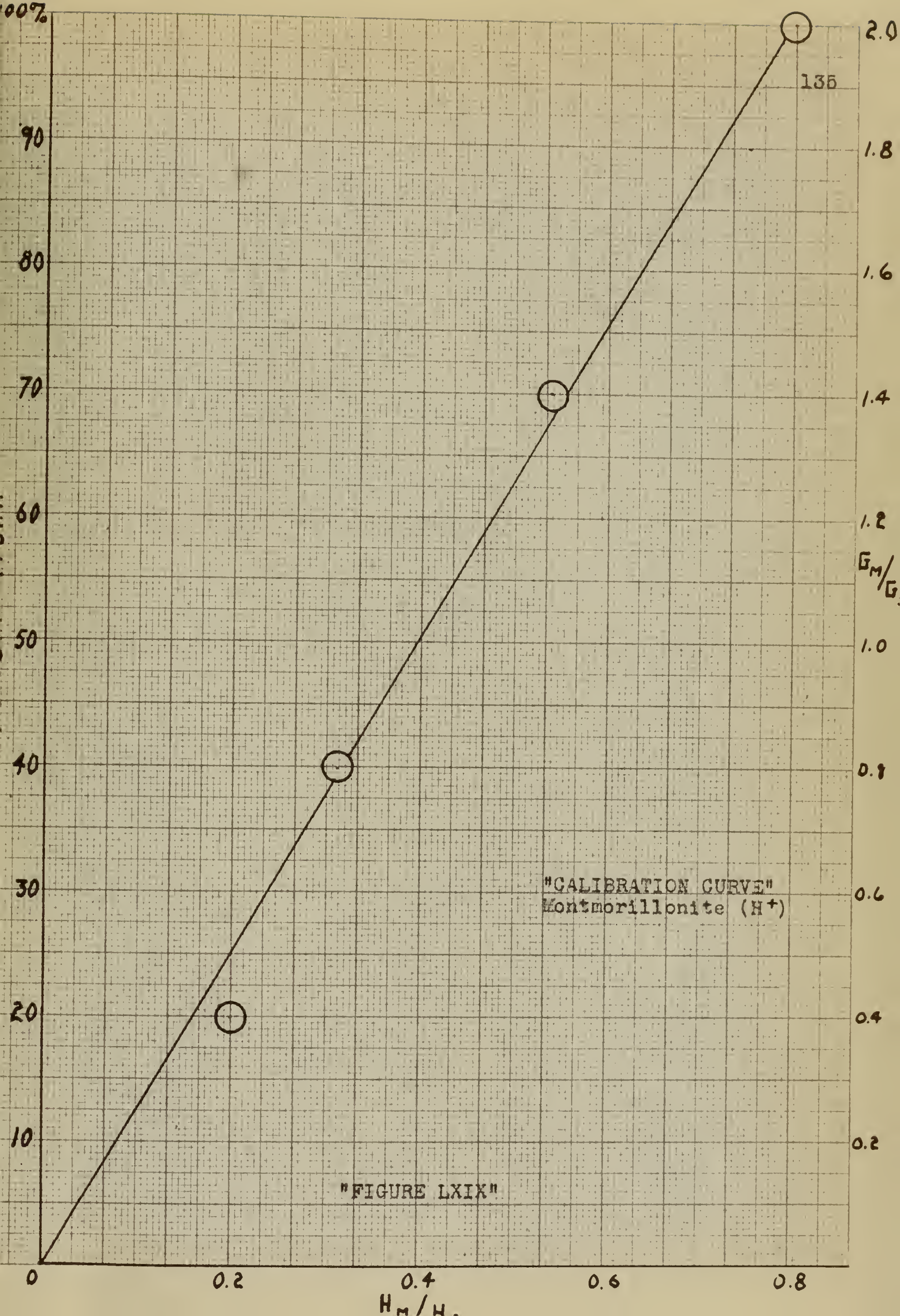
"FIGURE LXVIII"

Table 12

DATA ACCUMULATION

Montmorillonite (H^+) and Internal-Standard

	G_M/G_S		Height of Peak			Ave.	H_M/H_S
M-I	2.00	Mont.	5.7	5.4	5.9	5.6	0.80
		Int. Std.	6.7	7.5	6.9	7.0	
M-II	1.40	Mont.	3.6	4.0	3.4	3.6	0.54
		Int. Std.	6.6	7.0	6.5	6.7	
M-III	0.80	Mont.	1.5	1.6	1.7	1.6	0.31
		Int. Std.	5.5	5.3	5.0	5.2	
M-IV	0.40	Mont.	1.7	1.7	1.4	1.7	0.20
		Int. Std.	8.0	8.6	8.3	8.3	


100%
90
80
70
60
50
40
30
20
10
0
0.2
0.4
0.6
0.8
H_M/H
2.0
1.8
1.6
1.4
1.2
G_M/G
1.0
0.8
0.6
0.4
0.2
"CALIBRATION CURVE"
Montmorillonite (H^+)

"FIGURE LXIX"

APPENDIX D

Step-by-Step Procedure Recommended for Use in Analyzing Clay Minerals by X-ray Diffraction

Outline of Procedure for
Use in X-ray Diffraction
Analysis of Clay Minerals

I. Samples:

a) Standards. Standard samples are available from Wards Natural Science Establishment, Inc. A ready reference for standards listed by looale from which taken may be found in "Reference Clay Minerals A. P. I. Research Project 49".

b) Natural. Natural samples taken for analysis need not be undisturbed samples for x-ray diffraction use. It is necessary to dry the sample at 110° C. for a minimum of three hours or until all but crystalline moisture is evaporated.

II. Procedure for X-ray Analysis:

a) Use only samples that have been dried by furnace at 110° C.

b) Grind the sample and sieve with mechanical shaker retaining only that portion that passes a 325 mesh sieve. The balance can be ground by mortar and pestle and re-sieved.

c) The samples are now mounted in the x-ray diffractometer sample holder as follows:

1) place holder face down on a glass slide.

2) tamp an excess of sample into the holder rectangle using a small spatula.

3) remove excess sample with a razor blade.

4) place a second glass slide, cut to the size of the holder, on the back and turn the two slides and holder over.

5) remove the original slide and tape the holder and remaining slide together below the rectangle.

6) insert this unit into the goniometer holder.

d) Spectrometer settings for best results in clay mineral analysis using copper radiation with a nickel filter are:

MA - 15

KVP - 70

Rate Meter: SF - 8
M - 0.6
TC - 8

Scanning Speed: 1^{o} (2θ)/Minute

e) Perform a complete scan of the sample from 10^{o} to 70^{o}(2θ) obtaining a strip chart from the automatic recorder.

f) Using the (2θ) locations of the peak intensities from (e) above, calculate the d spacings by the Bragg equation $n\lambda = 2d \sin \theta$ and list in decreasing order.

g) Designate the greatest intensity peak as I_{100}

and by planimetering the other peaks, list in order (I_{90} , I_{80}, I_{50}, etc.) with their proper d value.

h) Group the resultant list of d values in accordance with the Hanawalt Grouping Scheme (Ref. page 393, Klug and Andrews, "X-ray Diffraction Procedures").

i) Qualitatively choose the type of clay mineral or other constituents of the sample by comparing (h) with the ASTM cards or by use of the "Cumulative Alphabetical and Grouped Numerical Index of X-ray Diffraction Data" book published by ASTM. A large number of clay minerals are included in this book under Scetion III.

j) For quantitative analysis procede as follows:

1) prepare sample by powdering to < 325 mesh sieve as before.

2) remove organic material: oxidizing with 0.06 H_2O_2 by boiling 16 grams for 5 minutes in 30 cc of the H_2O_2 - centrifuge - pour off supernate - treat with 20 cc of 0.17 N HCL by stirring for 2 minutes in a high-speed mechanical stirring machine - centrifuge - pour off supernate - wash and centrifuge three times with distilled water.

3) perform a spectrometer run and compare with original of step (e) marking on the original

the intensity peaks that have been removed by elimination of the organic material.

4) with the pure mineral or standard that corresponds to the unknown sample (found by comparison under step(i), plot a calibration curve using the internal standard technique of x-ray diffraction (Ref. page 419, Klug and Andrews "X-ray Diffraction Procedures"). Special attention should be paid to choice of the internal standards to prevent overlap of peaks. The ordinate of the curve is plotted as relative weights and the abscissa as relative resulting peak intensity taken from x-ray diffraction strip charts.

5) with the internal standard used in (4) above, mix a sample for quantity determination of the unknown sample as follows:

1 gram - Unknown quantity clay

1 gram - Internal standard

1 gram - Diluent.

6) after thorough mixing for one hour, prepare a strip chart of this sample through a range covering the I_{100} intensity peak of the internal standard and the I_{100} peak of the clay.

7) measure the peaks of (6) above and set up a ratio $H_{clay}/H_{standard}$. Enter the calibration curve with this ratio and therein find the

weight ratio represented and from this calculate the clay quantity. If a diluent was used in preparing the calibration curve, the per cent of clay mineral present in a compound may be taken directly from the curve.

APPENDIX E

Analysis of Unknown Clay Mineral Sample Using X-ray Diffraction Procedure

X-ray Diffraction Analysis of Clay Samples from the St. Lawrence Seaway Site

A. Samples

Two samples were received by the Division of Sanitary Engineering and Soil Mechanics, Department of Civil Engineering, Rensselaer Polytechnic Institute, from the New York State Soil Mechanics Laboratory. Information received stated that the samples came from the proposed construction site of the St. Lawrence Seaway near Messena, New York.

The samples were identified as follows:

Sample No. 1 - S - RLUH 3A - 16
59 + 100 ℄
28.2′ - 28.6′

Sample No. 2 - Long Sault Test Trench
Sample 7
Depth 17.1 feet

In appearance, the samples were both a dark clay-like material, sticky, and without appreciable large granular material.

B. X-ray Procedure

1. Qualitative analysis was accomplished by mounting thoroughly dried portions of the samples in fine powder form ($<$ 325 mesh sieve size) in the x-ray spectrometer-holder and running a diffraction strip chart through the range of 10° to 70° (2θ) for each sample (see Figure 1 & 2).

Organic material was then removed from the original samples by treatment with H_2O_2 and HCl in accordance with the standard procedure of the International Society of Soil Science. A diffraction strip chart run after organic removal indicated the peak intensities that were removed by this procedure.

Identification of the materials contributing to the balance of the peaks was made by use of the ASTM Cumulative X-ray Diffraction Index. Lattice spacings and relative peak intensities from the strip charts were compared to the known materials from this book.

As indicated on Figures 1 and 2, the main components of the sample were found to be similiar to: Illite (standard Morris, Illinois, Illite listed by API Research Project 49), Talc, and Organic material.

2. Quantitative analysis was performed only on the main constituent, the Illite, by use of the internal standard technique. The standard chosen was Zinc Sulfite with a diluent, Calcium Chloride. Relative weights of a range of mixtures of standard Morris, Illinois, Illite, internal standard, and diluent were plotted against resultant peak intensities from the diffraction strip charts to obtain a calibration curve. Measured weights of the St. Lawrence samples were then mixed with standard and diluent and a strip chart prepared for each. Relative peak heights were then calculated, and, using the calibration curve, the per cent of Illite was obtained.

An approximation of the components is as follows:

Material similiar to Morris, Illinois, Illite 30 - 40%, Talc 20 - 30%, Organic material 10 - 20%, Unknown 10 - 20% for both St. Lawrence Seaway samples.

The material not included herein such as: diffraction charts, calibration curves, data on sample mixtures, etc., is on file in the Division of Sanitary Engineering and Soil Mechanics, Rensselaer Polytechnic Institute.


90
80
70
60
50
40
30
20
10
0
I
90°
85°
80°
75°
70°
65°
60°
55°
50°
45°


SAMPLE: No. 2 St. Lawrence Seaway
Spectrometer Data:
Rad Cu Filter Ni
KVP 70 MA 15
Scan Speed 1° (2θ)/Min
SF 8 M 0.6 TC 8
"FIGURE 2"
I - Illite
T - Talc
O - Organic Material
90
80
70
60
50
40
30
20
10
0
50°
45°
40°
35°
30°
25°
20°
15°
10°
2θ

Thesis 33135
P768 Powell
The use of x-ray diffraction procedures in analysis of clay minerals.